

Adsorption Simulation Software

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**The Development of Adsorption Simulation Software
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FINAL REPORT

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ABSTRACT

Research is currently being undertaken at the Canadian Centre for Mineral and Energy Technology to investigate the possibility of removing unwanted heteroatomic compounds from the feedstock during the early stages of fuel production via an adsorption process using zeolites. Since nitrogenous compounds in particular make the hydrotreating process very expensive, the realization of this possibility could significantly reduce refining costs. Currently the research to determine appropriate adsorbent design is done primarily through the use of comparative column adsorption experiments which are costly and time consuming to perform. In this report computer simulation software is developed for both batch and column adsorption processes that can be used to significantly reduce the experimental effort required.

INTRODUCTION

In the early stages of fuel production the feedstock must be hydrotreated in order to remove the nitrogenous and sulfurous compounds which can poison the catalysts (1,2) and promote gum formation in the final product (3,4). The nitrogenous compounds are the most troublesome since they are more resistant to the hydrotreating process than the sulfurous compounds and thus dictate the process severity. Under these conditions a fraction of the starting material is lost through extensive cracking which produces unwanted gases. The problem is compounded by the fact that the whole feed is hydrotreated even though only a small fraction of the feed contains nitrogen. Therefore, if a more efficient and cost effective process for removing nitrogenous compounds could be developed, refining costs would be significantly reduced, to the obvious benefit to the petrochemical industry.

Scientists at the Canadian Centre for Mineral and Energy Technology (CANMET) (5) have suggested that in certain cases it may be more economical to selectively remove the nitrogenous compounds via an adsorption process using molecular sieve zeolites.

Investigations on the design of effective adsorbents are currently carried out through the costly and time consuming method of trial and error comparison between the results of many column adsorption experiments in which some of the many variables effecting column performance are systematically changed. The pace and efficiency of the research could be greatly increased if CANMET scientists could use the tool of computer simulation to replace much of the experimental work. A reliable computer simulator could be used to approximate the effects of changes in the variables and the experimental work could then be largely limited to investigations at or near the optimum conditions indicated by the simulation results.

In this report, although we are primarily interested in column adsorption, software for the simulation of both batch and column adsorption is developed. The batch simulator is developed to aid in determining certain parameters to be used with the column simulator. The use of this software could be very useful to the research being done at CANMET.

In the following section we will briefly discuss some of the factors affecting the batch and column adsorption processes. Then in the following section we will give a review of the pertinent literature.

FACTORS AFFECTING THE PERFORMANCE OF BATCH AND COLUMN ADSORPTION PROCESSES

In the simple batch process an amount of adsorbent material in the form of small particles (pellets or powder) is added to an Erlenmeyer flask closed with a stopper and filled with a liquid containing adsorbate(s). The system is agitated to ensure uniform concentration in the bulk fluid (i.e. the fluid remaining outside of the adsorbent particles). The adsorption capacity of the adsorbent toward a particular adsorbate in the liquid is determined experimentally by measuring the concentration of the adsorbate in the bulk fluid as a function of time with the use of chromatographic analysis.

The adsorption column consists of a metal tube packed with an adsorbent material through which a feedstream is pumped upward. In the ongoing studies the feedstream and the liquid used in the batch process consists of one or more heteroatomic compounds dissolved in an organic solvent. The performance of the column with respect to a particular adsorbate is evaluated from the "breakthrough curve" of the adsorbate which is simply the graphic representation of the concentration of adsorbate in the eluted feedstream as a function of time (or total eluted liquid).

The extent of adsorption and the shape of the concentration vs. time curves for both processes is determined by a multitude of factors of which many are interrelated (6,7,8,9). Some of these are related to characteristic properties of the particular adsorbate-solvent-adsorbent combination under consideration such as the affinity of the adsorbate for the surface of the adsorbent and the nature of the equilibrium conditions. Other factors, specific to the adsorbate include concentration, molecular size, weight, and shape, polarity, and the nature of background or competitive adsorbates. Factors pertinent to the adsorbent include the particle size and the physico-chemical nature and size of the particle's adsorbing surface. Finally, system parameters such as the temperature, degree of agitation (batch process), length of column and superficial flow velocity of the feedstream through the bed (column process), can all have a marked influence.

MATHEMATICAL MODELLING OF ADSORPTION

Before proceeding with a brief review of the mathematical modelling of adsorption it will be instructive to examine the mass transfer mechanisms involved.

In the case of a typical adsorbent such as activated carbon there are essentially three consecutive mass transport steps associated with the adsorption of solutes from solution. The first step, bulk transport of solute in the solution phase is usually rapid because of mixing and/or advective flow, however, in the case of column processes radial or axial diffusion may be significant. The second step, film transport, involves diffusion of the solute through a hypothetical "film" or hydrodynamic boundary layer. Except for a small amount of adsorption that occurs on the exterior of the adsorbent particle, the solute then must diffuse within the pore volume of the adsorbent and/or along pore wall surfaces to an active adsorption site (intraparticle transport). In some cases these three mass transport steps may be followed by another in which the adsorbed solute diffuses through the solid portions of the adsorbent.

In the case of adsorbents such as commercial zeolites another mass transport step must be considered. As synthesized, commercial zeolite crystals are quite small (typically 1-10 microns) (10) and to prepare a practically useful adsorbent these crystals must be formed with the use of a binding material into a macroporous pellet of suitable dimensions, porosity, and mechanical strength. Such a composite pellet offers two distinct diffusional resistances to mass transfer: the micropore diffusional resistance of the individual zeolite crystals and the macropore resistance of the extracrystalline pores.

The mathematical models that have been developed differ primarily in their assumptions as to which mass transfer steps are rate limiting, the importance of and the representation of thermodynamic effects (including the nature of the equilibrium conditions), the form of the coupling mechanisms (driving forces) to be used in the mass and/or heat balance equations, and the form of the initial and boundary conditions. Simplifications that are often made include: the treatment of the adsorbent particle as a homogeneous solid irrespective of its porous structure, the assumption of parabolic concentration profiles within the adsorbent particle or the use of a "lumped" model for the adsorbent particle which avoids the necessity of solving the partial differential equations for diffusion within the particle, the use of linear equilibrium isotherms, and the assumption of plug flow. Ruthven (10) gives a broad range of models ranging from single component isothermal batch adsorption to multicomponent non-isothermal column adsorption.

We shall now review some of the analytical work that has been done to obtain solutions to some of the mathematical models.

LITERATURE REVIEW OF ANALYTIC SOLUTIONS

In most cases the analytic solutions that have been obtained apply to single component models that treat the adsorbent particles as equivalent spheres, assume isothermal conditions, linear equilibrium isotherms, constant diffusivities, and plug flow (column models). The major differences between the models are in the representation of the mass transfer rates and/or the inclusion or omission of an axial dispersion term.

Crank (11) gives solutions for both the infinite and finite batch system models assuming a single diffusional resistance (monodisperse sorbent) and constant diffusivity (note that the infinite batch system is equivalent to a single particle system with a constant external fluid concentration). Garg and Ruthven (12) and Kocirik et al. (13) extended the finite batch analysis to account for a particular concentration dependent diffusivity. Ruckenstein et al. (14) appear to have been the first to develop a solution to an infinite batch system model in which the external film resistance and both the macropore and micropore diffusional resistances are treated (bidisperse sorbent). Essentially the same problem was considered by Ma and Lee (15) and by Lee (16) who extended the analysis to include the finite batch case.

Rice (17) gives approximate solutions for both batch and column adsorbers using Gluekauf's (18) linear driving force approximation (LDFA) in which the rate of mass transfer across the particles' exterior surface is assumed to be proportional to the distance the system is from equilibrium. He also compares the solutions with experimental data. Interestingly, Liaw et al. (19) show that the common practice of assuming a parabolic concentration profile leads in fact directly to the LDFA. Do and Rice (20) show that for the case of the single particle model the LDFA has rather restricted validity and Do and Mayfield (21) give an improved approximation.

For monodisperse sorbents, solutions for the breakthrough curve have been derived for various mass transfer resistances. Furnas (22) and Walter (23,24) derived solutions by considering only the external film resistance. Solutions were derived for intraparticle resistance only and both intraparticle resistance and external film resistance by Rosen (25,26). Rasmuson and Neretnieks (27) obtained results for these cases with the inclusion of axial dispersion.

For the case of bidisperse adsorbents Kawazoe and Takeuchi (28) have obtained a solution for plug flow and external film resistance. Haynes (29) and Rasmuson (30) obtained solutions for the axially dispersed case as did Friedrich et al. (31) for a pulse input. Cen and Yang (32) have developed simpler solutions by assuming parabolic profiles in both the macropores and the micropores.

When the equilibrium relationship is non-linear it is generally not possible to determine a general analytic solution for the breakthrough curve. However, solutions for a number of special cases have been obtained, primarily with the irreversible (rectangular) isotherm. Limiting cases of solid diffusion control and pore diffusion control were solved by Cooper (33) and by Cooper and Libermann (34) while the solution for combined pore diffusion and external mass transfer resistance was obtained by Weber and Chakravorti (35).

LITERATURE REVIEW OF NUMERICAL SOLUTIONS

Numerical solutions for isothermal models have been obtained by many authors of which the following are representative.

Marcussen (36) has solved an infinite batch model with external film and pore resistance for a single adsorbing species in an inert solvent. Neretnieks (37) has solved a finite batch model for a similar system for external film resistance and combinations of pore and surface diffusion

resistance. Liapis and Rippin (38) and Santacesaria et al. (39) have solved a multicomponent model for trace adsorption from a finite bath with external film and pore diffusion resistance. Mansour et al. (40) have solved a similar non-equilibrium model.

For the case of isothermal column processes the following are some who have investigated single component adsorption: Zwiebel et al. (41) for fluid film resistance, Garg and Ruthven (42) for solid film resistance (i.e. resistance at the adsorption surface), Tien and Thodos (43) for external film and solid film resistance, Kyte (44) for solid diffusion resistance and Carter and Hussain (45) for pore diffusion resistance.

A number of solutions to multicomponent models assuming various resistances have been obtained. Crittenden and Weber (46) have solved a trace model with external film and surface diffusion resistances. Liapis and Rippin (47), Balzli et al. (48) and Liapis and Litchfield (49) have included external film and pore diffusion resistances and axial dispersion. Mansour et al. (50) have solved a non-equilibrium model with external film and pore resistances without axial dispersion. In these works the models have all incorporated analytic multicomponent adsorption expressions.

Hsieh et al. (51) have developed a more general solution method for equilibrium relationships of the Langmuir type and Wang and Tien (52), Tien (53) and Moon and Lee (54) have all incorporated the ideal adsorbed solution theory (IAS) into their solution procedures to estimate the required multicomponent equilibrium data. Sheindorf et al. (55) have outlined a method of constructing the necessary multicomponent data for cases where the single component isotherms are of Freundlich type.

Santacesaria et al. (56) and Moon and Lee (54) have developed and solved lumped models and Hall et al. (57) and Katoh et al. (58) have developed numerical solution procedures for fixed bed adsorption under constant pattern conditions.

Solutions to non-isothermal models have been obtained by a number of authors including Cooney (59), Marcussen (60), Raghavan and Ruthven (61), Liapis and Crosser (62) and Nagel et al. (63).

In the following sections we shall discuss our development of the adsorption simulation software for the work being done at CANMET.

MAJOR ASSUMPTIONS AND CHOICE OF MATHEMATICAL MODEL

To begin we shall give the major assumptions that we make regarding the experimental conditions and our subsequent choice of a suitable mathematical model.

Since the adsorption columns in the ongoing experiments are not thermally isolated but are in contact with the air (at room temperature) and, since the adsorbate concentrations are low (typically 10^{-3} moles per litre) so that the temperature contribution due to the exothermic adsorption reaction is likely to have a negligible effect, we shall assume isothermal conditions in the columns. Also, since the concentrations are low we shall assume that the diffusion rates of each adsorbate are independent of any other adsorbate.

The next assumption that we make relates to the mass transfer mechanisms within the zeolite adsorbent particles. Since a reasonably large throughput would be necessary for an industrial scale process and this prevents the pellets from being too small we shall assume that the macropore diffusional resistance is dominant and that the micropore diffusional resistance can be ignored. In any particular case the validity of this assumption can be determined from batch experiments using different particle sizes (10) or from analytic criteria such as those of Garg and Ruthven (64) or Dogu and Dogu (65).

Since the adsorption reaction at the particle surface is rarely rate limiting we shall also make the common assumption that local equilibrium conditions apply between the solid (adsorbed) and fluid phases of the adsorbates in the pore spaces.

The major assumptions that we have made underlie the so-called "pore diffusion" model that has been used by Liapis and Rippin (47) and Liapis and Litchfield (49) to simulate column adsorption. These authors use an approach first suggested by Liapis and Rippin (38) to obtain the effective pore diffusion coefficients that are required for the adsorbates. Rather than obtaining values from correlations in the literature (although these may be used as initial estimates if available) a pore diffusion batch model is solved and the predictions are compared with data from simple multicomponent batch experiments covering the expected concentration ranges. The values of the pore diffusion coefficients are adjusted until acceptable agreement is reached and these values are then used in the column model. The details and mathematical formulation of both models are given below. Note that the non-dimensionalization of Liapis and Litchfield above is employed but no coordinate transformation involving the radial variable is applied.

THE BATCH MODEL

Adsorption is considered from a liquid containing n_{sor} dissolved components ($n_{sor} \geq 1$). The mass transfer between the external and pore fluids is assumed to take place across a thin film or boundary layer surrounding each particle. The concentration in the external fluid in the reservoir is assumed to be uniform outside of the film regions. Under these conditions a non-dimensional differential mass balance for each component i ($1 \leq i \leq n_{sor}$) in the fluid phase gives

$$\frac{dC_{\Delta}}{dT} = \frac{\epsilon - 1}{\epsilon} \frac{A_0}{D_{p1} r_0} \frac{3}{2} (C_{\Delta}(T) - C_{pi}(1, T)) K_{fi} \quad (1)$$

with initial conditions given by

$$C_{\Delta}(0) = 1. \quad (2)$$

A non-dimensional mass balance obtained by considering mass transfer by macropore diffusion within the particles (which are treated as equivalent spheres with spherically symmetric concentration profiles) under local equilibrium conditions gives

$$\epsilon_p \frac{c_{\alpha}}{c_{01}} \frac{\partial C_{pi}}{\partial T} + \frac{c_{\alpha}^*}{c_{01}} \frac{\partial C_{pi}}{\partial T} = \frac{4\pi\epsilon_p D_{pi} c_{\alpha}}{D_{p1} c_{01}} \left(\frac{\partial^2 C_{pi}}{\partial R^2} + \frac{2}{R} \frac{\partial C_{pi}}{\partial R} \right) \quad (3)$$

with initial and boundary conditions given by

$$C_{pi}(R, 0) = 0 \quad \text{for } 0 \leq R \leq 1 \quad (4)$$

$$\frac{\partial C_{pi}}{\partial R} = \frac{Sh_{pi}}{2} (C_{\Delta}(T) - C_{pi}(1, T)) \quad \text{for } R = 1, T > 0 \quad (5)$$

$$\frac{\partial C_{pi}}{\partial R} = 0 \quad \text{for } R = 0, T > 0. \quad (6)$$

Also required are the equilibrium isotherms for each component in the following functional form

$$C_i = \frac{1}{c_{s0i}} f_i(c_{p1}, c_{p2}, \dots, c_{pnsor}) = \frac{1}{c_{s0i}} f_i(c_{01}C_{p1}, c_{02}C_{p2}, \dots, c_{0nsor}C_{pnsor}). \quad (7)$$

To simplify the solution procedure we make use of eqn.7 and the the chain rule to obtain the following equivalence

$$\frac{c_{s0i}^*}{c_{01}} \frac{\partial C_i}{\partial T} = \frac{1}{c_{01}} \sum_{j=1}^{nsor} \frac{\partial f_i}{\partial C_{pj}} \frac{\partial C_{pj}}{\partial T}. \quad (8)$$

Thus, instead of eqn.3 we use the following equivalent form

$$\left(\epsilon_p \frac{c_{0i}}{c_{01}} + \frac{1}{c_{01}} \frac{\partial f_i}{\partial C_{pi}} \right) \frac{\partial C_{pi}}{\partial T} + \frac{1}{c_{01}} \sum_{j=1}^{nsor} \frac{\partial f_i}{\partial C_{pj}} \frac{\partial C_{pj}}{\partial T} = \frac{4\pi\epsilon_p D_{pi} c_{0i}}{D_{p1} c_{01}} \left(\frac{\partial^2 C_{pi}}{\partial R^2} + \frac{2}{R} \frac{\partial C_{pi}}{\partial R} \right). \quad (9)$$

THE COLUMN MODEL

Adsorption is considered from a liquid containing $nsor$ dissolved components ($nsor \geq 1$) flowing through a fixed bed of uniform size and homogeneous structure with a constant superficial flow velocity. The mass transfer between the external and pore fluids is assumed to take place across a thin film or boundary layer surrounding each particle. The concentration in the external fluid in the column is assumed to be radially constant outside of the film regions but axial diffusion is considered. Under these conditions a non-dimensional mass balance for each component i ($1 \leq i \leq nsor$) in the fluid phase of the column gives

$$\frac{\partial C_{\Delta}}{\partial T} = \frac{\epsilon - 1}{\epsilon} \frac{A_0}{D_{p1} r_0} 3 (C_{\Delta}(X, T) - C_{pi}(1, X, T)) K_f + \frac{A_0 V}{\epsilon L D_{p1}} \left(\frac{1}{Pe_i} \frac{\partial^2 C_{\Delta}}{\partial X^2} - \frac{\partial C_{\Delta}}{\partial X} \right) \quad (10)$$

with initial and boundary conditions given by

$$C_{\Delta}(X, 0) = 0 \quad \text{for } 0 \leq X \leq 1 \quad (11)$$

$$C_{\Delta}(0, T) = \frac{C_{i, in}}{C_{0i}} + \frac{1}{Pe_i} \frac{\partial C_{\Delta}}{\partial X} \quad \text{for } X = 0, T > 0 \quad (12)$$

$$\frac{\partial C_{\Delta}}{\partial X} = 0 \quad \text{for } X = 1, T > 0. \quad (13)$$

A non-dimensional mass balance obtained by considering mass transfer by macropore diffusion within equivalent spherical particles under local equilibrium conditions gives

$$\epsilon_p \frac{c_{0i}}{c_{01}} \frac{\partial C_{pi}}{\partial T} + \frac{c_{s0i}^*}{c_{01}} \frac{\partial C_i}{\partial T} = \frac{4\pi\epsilon_p D_{pi} c_{0i}}{D_{p1} c_{01}} \left(\frac{\partial^2 C_{pi}}{\partial R^2} + \frac{2}{R} \frac{\partial C_{pi}}{\partial R} \right) \quad (14)$$

$$C_{pi}(R, X, 0) = 0 \quad \text{for } 0 \leq R \leq 1, 0 \leq X \leq 1 \quad (15)$$

$$\frac{\partial C_{pi}}{\partial R} = \frac{Sh_i}{2} (C_{di}(X,T) - C_{pi}(1,X,T)) \text{ for } R = 1, 0 \leq X \leq 1, T > 0 \quad (16)$$

$$\frac{\partial C_{pi}}{\partial R} = 0 \text{ for } R = 0, 0 \leq X \leq 1, T > 0. \quad (17)$$

Again, as in the batch model, an equilibrium isotherm in the form of eqn.7 is required for each component and eqn.9 is used instead of eqn.14 in the solution procedure (realizing of course that C_{pi} is now also implicitly dependent on X).

BATCH MODEL SOLUTION PROCEDURE

We shall now examine the solution procedures for the model equations beginning with the batch model.

For each of the n_{sor} adsorbate species the model consists of an ordinary differential equation (ODE) with dependent variable C_{di} and independent variable T (eqn.1) coupled with a partial differential equation (PDE) with dependent variable C_{pi} and independent variables R and T (eqn.9). The coupling between the equations occurs through the terms involving the difference between the free fluid concentration and the particle surface concentration in eqn.1 and eqn.5.

The usual method of solution for a system such as this is to first reduce the PDE in R and T to an ODE in T only by "discretizing" the R dependence in the PDE and its boundary conditions. This reduces the system to a standard initial value problem for which there are a number of integration software packages available.

The most common methods for discretizing the spatial (R) dependence in these types of models are the methods of orthogonal collocation and finite differences (see for example Villadsen and Michelsen (66) and Smith (67) for a detailed introduction to these methods).

We note here that we are speaking in particular of ordinary (i.e. global) collocation (in which one polynomial is used to approximate the solution over the entire domain) rather than more specialized methods such as collocation on finite elements (in which a different polynomial can be used over each element of a suitably sub-divided domain) or methods using adaptive grids.

In the literature it is generally claimed that for a given accuracy that collocation requires the least computer time. However, as noted in Finlayson (68) this depends on the nature of the solution (especially on the continuity of the higher derivatives) and that for problems with steep gradients finite differences or a more specialized method is preferred.

During the course of this work we developed simulators for both the batch and column models using both (global) collocation and finite differences. We ran several simulations using both methods and evaluated the solutions obtained on the basis of physical realism and computational efficiency. From our experience we judged that either of the collocation or finite difference methods were suitable for the batch model but that the finite difference method was preferable to the collocation method in the case of the column model (see the section "CODE VERIFICATION" for more details) and hence we have chosen to submit the finite difference simulators to EMR. Therefore, the development of these simulators will be emphasized in this report.

To discretize the R dependence of eqn.9 i.e. the term

$$\left(\frac{\partial^2 C_{pi}}{\partial R^2} + \frac{2}{R} \frac{\partial C_{pi}}{\partial R} \right) \quad (18)$$

using finite differences we begin by subdividing the domain $0 \leq R \leq 1$ with $NRPT$ equally spaced points DR units apart where $DR = 1/(NRPT - 1)$. In addition we shall make use of external grid points at $0 - DR$ and $1 + DR$ to deal with the boundary conditions (as we shall see). We label the ordinate $R = 0$ as point R_1 , $R = DR$ as point R_2 , ..., $R = (n - 1) \cdot DR$ as point R_n , ..., and $R = 1$ as point R_{NRPT} . (Note that $R = 0$ corresponds to the centre of the particle while $R = 1$ corresponds to the surface.)

We shall now discuss the discretization of the first and second derivative terms in eqn.18 for a point R situated away from the boundaries.

An approximation to the value of the concentration $C_{pi}(R + DR, T)$ near $C_{pi}(R, T)$ is given by a Taylor series in R i.e.

$$\begin{aligned} C_{pi}(R + DR, T) = & C_{pi}(R, T) + \frac{\partial C_{pi}(R, T)}{\partial R} (DR) + \frac{1}{2!} \frac{\partial^2 C_{pi}(R, T)}{\partial R^2} (DR)^2 \\ & + \frac{1}{3!} \frac{\partial^3 C_{pi}(R, T)}{\partial R^3} (DR)^3 + \frac{1}{4!} \frac{\partial^4 C_{pi}(R, T)}{\partial R^4} (DR)^4 + \dots \end{aligned} \quad (19)$$

Similarly for $C_{pi}(R - DR, T)$ we have

$$\begin{aligned} C_{pi}(R - DR, T) = & C_{pi}(R, T) - \frac{\partial C_{pi}(R, T)}{\partial R} (DR) + \frac{1}{2!} \frac{\partial^2 C_{pi}(R, T)}{\partial R^2} (DR)^2 \\ & - \frac{1}{3!} \frac{\partial^3 C_{pi}(R, T)}{\partial R^3} (DR)^3 + \frac{1}{4!} \frac{\partial^4 C_{pi}(R, T)}{\partial R^4} (DR)^4 + \dots \end{aligned} \quad (20)$$

Subtracting eqn.20 from eqn.19, rearranging and dropping residual terms gives a central difference approximation to the first derivative at the point R i.e.

$$\frac{\partial C_{pi}}{\partial R}(R, T) \sim \frac{C_{pi}(R + DR, T) - C_{pi}(R - DR, T)}{2DR} \quad (21)$$

The residual terms that have been dropped are referred to as the "truncation error" and consist of

$$-\frac{1}{6} \frac{\partial^3 C_{pi}(R, T)}{\partial R^3} (DR)^2 + \text{terms in higher powers of } DR. \quad (22)$$

Reflecting the power of the leading error term the truncation error is said to be of "order" $(DR)^2$. Thus, the approximation eqn.21, is referred to as being accurate to second order.

Similarly, if eqn.19 and eqn.20 are added and rearranged the following second order accurate formula for the second derivative can be obtained

$$\frac{\partial^2 C_{pi}}{\partial R^2}(R, T) \sim \frac{C_{pi}(R + DR, T) - 2C_{pi}(R, T) + C_{pi}(R - DR, T)}{(DR)^2} \quad (23)$$

Now at a point $R = R_n$ where $1 < n < NRPT$ which is one of the interior equally spaced points that we have already defined we can "discretize" or approximate the spatial term with the use of these formulae as

$$\left(\frac{\partial^2 C_{pi_n}}{\partial R^2} + \frac{2}{R} \frac{\partial C_{pi_n}}{\partial R} \right) C_{pi_{n+1}} \left(\frac{1}{(DR)^2} + \frac{1}{R_n DR} \right) - 2 \frac{C_{pi_n}}{(DR)^2} + C_{pi_{n-1}} \left(\frac{1}{(DR)^2} - \frac{1}{R_n DR} \right) \quad (24)$$

where we have used the shorter notation $C_{pi_{n+1}}$ for $C_{pi}(R_n + DR, T)$ etc. and where the notation $\partial C_{pi_n} / \partial R$ will be understood to mean the derivative of C_{pi} at the point R_n etc.

We shall now examine the discretization at the boundary points beginning with the boundary at $R = 0$ which has the condition $\partial C_{pi} / \partial R = 0$. To determine the behaviour of the term $(2/R) \partial C_{pi} / \partial R$ as R approaches 0 we make use of L'Hopitals rule i.e.

$$\lim_{R \rightarrow 0} \left(\frac{2}{R} \frac{\partial C_{pi}}{\partial R} \right) = \lim_{R \rightarrow 0} \frac{\frac{\partial C_{pi}}{\partial R}}{\frac{R}{2}} = \lim_{R \rightarrow 0} \frac{\frac{\partial}{\partial R} \left(\frac{\partial C_{pi}}{\partial R} \right)}{\frac{\partial}{\partial R} \left(\frac{R}{2} \right)} = 2 \frac{\partial^2 C_{pi}}{\partial R^2} \quad (25)$$

Since the concentration is symmetric about the point $R = 0$ the concentration at the external point $0 - DR$ equals the concentration at the first interior point $0 + DR$. Using this fact and the central difference approximation eqn.23 for the second derivative gives the following discretization of the spatial term at $R = 0$

$$\begin{aligned} \lim_{R \rightarrow 0} \left(\frac{\partial^2 C_{pi}}{\partial R^2} + \frac{2}{R} \frac{\partial C_{pi}}{\partial R} \right) &= 3 \frac{\partial^2 C_{pi1}}{\partial R^2} \\ &\sim 3 \left(\frac{2C_{pi2} - 2C_{pi1}}{(DR)^2} \right) \\ &= 6 \left(\frac{C_{pi2} - C_{pi1}}{(DR)^2} \right) \end{aligned} \quad (26)$$

For the point $R = 1$ we begin by discretizing the boundary condition eqn.5 using the external grid point at $1 + DR$ (i.e. R_{NRPT+1}) and the central difference equation for the first derivative viz.

$$\frac{\partial C_{piNRPT}}{\partial R} = \frac{C_{piNRPT+1} - C_{piNRPT-1}}{2DR} = \frac{Sh_i}{2} (C_{\infty} - C_{piNRPT}) \quad (27)$$

which can be solved directly for $C_{piNRPT+1}$ i.e.

$$C_{piNRPT+1} = C_{piNRPT-1} + (DR) Sh_i (C_{\infty} - C_{piNRPT}) \quad (28)$$

Thus substituting the rightmost side of eqn.27 for the first derivative in the spatial term eqn.18 and using eqn.28 to substitute for $C_{piNRPT+1}$ in the central difference expression for the second derivative we can obtain the following discretization at $R = 1$

$$\left(\frac{\partial^2 C_{piNRPT}}{\partial R^2} + \frac{2}{1} \frac{\partial C_{piNRPT}}{\partial R} \right) - C_{piNRPT} 2Sh_i \left(1 + \frac{1}{DR} + \frac{1}{Sh_i(DR)^2} \right) + C_{piNRPT-1} \frac{2}{(DR)^2} + C_e 2Sh_i \left(1 + \frac{1}{DR} \right) \quad (29)$$

With the use of the discretization procedure described above for eqn.9 an ODE in T is obtained at each of the $NRPT$ grid points for each of the $nsor$ adsorbates. As well eqn.1 gives one ODE in T for each adsorbate. Thus the batch model now consists of a system of $NEQB = nsor * (NRPT + 1)$ simultaneous equations in T plus initial conditions.

This system can be written using matrix notation as an initial value problem of the form

$$A \frac{\partial \vec{C}}{\partial T} = \vec{G}$$

$$\vec{C}(0) \text{ specified} \quad (30)$$

where the vector of unknowns $\vec{C}(T)$ consists of both C_{pi} 's and C_e 's. With judicious ordering of the equations the matrix A can be made to be of banded type (i.e. all non-zero elements lie on a narrow band of diagonals centred about the main diagonal) and we choose this form to optimize efficiency. The matrix A and the vectors $\vec{C}$ and $\vec{G}$ are given in component form in appendix A.1.

The initial value problem eqn.30 is solved with the use of the integration package LSODI which has been developed by the Lawrence Livermore National Laboratories for problems of this form (see Hindmarsh (69) for details of LSODI and other ODEPACK solvers).

COLUMN MODEL SOLUTION PROCEDURE

For each of the $nsor$ adsorbate species the model consists of a PDE with dependent variable C_e and independent variables X and T (eqn.10) coupled with a PDE with dependent variable C_{pi} and independent variables R , X and T (eqn.9). The coupling occurs through the terms involving the difference between the free fluid concentration at a point in the column and the corresponding particle surface concentration.

As noted earlier, the dependence of C_{pi} on X is only implicit when eqn.9 is used with the column model and hence the discretization of eqn.9 is performed exactly as in the batch case.

In eqn.10 we must discretize the X dependence i.e. the term

$$\left(\frac{1}{Pe_i} \frac{\partial^2 C_{di}}{\partial X^2} - \frac{\partial C_{di}}{\partial X} \right). \quad (31)$$

To begin we subdivide the domain $0 \leq X \leq 1$ with $MXPT$ equally spaced points DX units apart where $DX = 1/(MXPT - 1)$. In addition we shall use an external grid point at $0 - DX$ to deal with the boundary condition at $X = 0$. We label the ordinate $X = 0$ as point X_1 , $X = DX$ as point X_2 , ..., $X = (m - 1) * DX$ as point X_m , ..., and $X = 1$ as point X_{NRPT} . (Note that $X = 0$ corresponds to the inlet end of the column and $X = 1$ corresponds to the outlet.)

The discretization of the spatial term eqn.31 for a point away from the boundaries is analogous to that already derived for eqn.18 except that so-called "upstream" differencing is used for the first derivative. This only means that the first derivative is approximated by the first order accurate formula

$$\frac{\partial C_{di}}{\partial X}(R, X, T) \sim \frac{C_{di}(R, X, T) - C_{di}(R, X - DX, T)}{DX} \quad (32)$$

which can be obtained from a Taylor expansion similar to eqn.20. The purpose of using this approximation rather than the central difference formula is to reduce the possibility of oscillations in the solution for the free fluid concentrations when the gradients are large along the column length (for more information on this see for example Finlayson (68) and his discussion on the convective-diffusion equation). The result of using the second order central difference equation for the second derivative and eqn.32 for the first derivative gives the approximation

$$\begin{aligned} & \left(\frac{1}{Pe_i} \frac{\partial^2 C_{di}}{\partial X^2} - \frac{\partial C_{di}}{\partial X} \right) C_{di,m} \left(\frac{1}{Pe_i(DX)^2} \right) - C_{di,m} \left(\frac{2}{Pe_i(DX)^2} + \frac{1}{(DX)} \right) \\ & + C_{di,m-1} \left(\frac{1}{Pe_i(DX)^2} + \frac{1}{(DX)} \right) \end{aligned} \quad (33)$$

where $1 < m < MXPT$.

At the inlet $X = 1$ we have the boundary condition eqn.12. With the use of this equation, the external boundary point at $0 - DX$ and the central difference approximation to the first derivative we can write

$$\frac{\partial C_{di1}}{\partial X} \sim \frac{C_{di2} - C_{di0-1}}{2DX} = Pe_i \left(C_{di1} - \frac{C_{i,jn}}{C_{0i}} \right) \quad (34)$$

from which we can obtain

$$C_{di0-1} = C_{di2} - 2(DX)Pe_i \left(C_{di1} - \frac{C_{i,jn}}{C_{0i}} \right) \quad (35)$$

Using the rightmost side of eqn.34 to substitute for the first derivative in eqn.31 and using eqn.35 to substitute for C_{di0-1} in the central difference formulae for the second derivative gives the following discretization at $X = 0$

$$\begin{aligned} & \left(\frac{1}{Pe_i} \frac{\partial^2 C_{di1}}{\partial X^2} - \frac{\partial C_{di1}}{\partial X} \right) C_{di2} \left(\frac{2}{Pe_i + (DX)^2} \right) - C_{di1} \left(Pe_i + 2 \frac{1 + Pe_i(DX)}{Pe_i + (DX)^2} \right) \\ & + \frac{C_{i,jn}}{C_{0i}} \left(Pe_i + \frac{Pe_i(DX)}{Pe_i + (DX)^2} \right) \end{aligned} \quad (36)$$

At the outlet $X = 1$ we have the condition of zero slope of the free fluid concentrations i.e. $\partial C_{di}/\partial X = 0$. If we were to utilize an external grid point at $X = 1 + DX$ and use the central difference approximation to the first derivative to discretize this boundary condition we would have the result $C_{di,1+DX} = C_{di,1-DX}$ which implies symmetry of these concentrations about the boundary. However, from a physical perspective this can only be valid if DX is infinitesimally small, or for finite DX , at small times when both points are at zero concentration or at large times when the column has been saturated and both points are at the initial feedstream concentrations. Therefore instead of using central difference approximations for the derivatives we should use one sided approximations at this boundary. Actually, since the first derivative is zero at the boundary (and we are not going to use a central difference formula for the second derivative there) we would normally require only a one sided approximation for the second derivative, however as will soon be seen, it is useful to obtain the one sided formula for the first derivative as well at this point.

To obtain an appropriate second order accurate approximation to the first derivative we simply subtract and rearrange the Taylor series for $C_{di}(X - DX, T)$ and $C_{di}(X - 2X, T)$ (each having the same form as eqn.20) and drop the appropriate truncation error terms. The result taken at the boundary gives

$$\frac{\partial C_{diMXPT}}{\partial X} \sim \frac{-3C_{diMXPT} + 4C_{diMXPT-1} - C_{diMXPT-2}}{2DX} = 0 \quad (37)$$

from which we obtain

$$C_{diMXPT} = \frac{4C_{diMXPT-1} - C_{diMXPT-2}}{3} \quad (38)$$

A second order accurate one sided formula for the second derivative can be constructed in a similar way if one also uses the Taylor series for $C_{di}(X - 3X, T)$. The following is then obtained at the boundary

$$\frac{\partial^2 C_{diMXPT}}{\partial X^2} \sim \frac{2C_{diMXPT} - 5C_{diMXPT-1} + 4C_{diMXPT-2} - C_{diMXPT-3}}{(DX)^2} \quad (39)$$

Hence the discretization of the spatial term eqn.31 at $X = 1$ is simply the left side of eqn.39 divided by Pe_i . Unfortunately, we have found that the use of this discretization appears to introduce a numerical instability into the solution. Typically this instability grows rather slowly but eventually becomes manifest as oscillatory behaviour in the concentrations that begins at the outlet end of the column and works back toward the inlet end. While we found that this behaviour could be controlled by using a smoothing algorithm every few time steps it would obviously be better to avoid this procedure if possible since the rigor of the solution procedure is thrown into doubt i.e. different smoothing techniques can give significantly different results and there is no way of telling which is closest to the real solution. Fortunately, we were able to find an alternative method for handling the boundary condition at the outlet in a manner that eliminates the instability and yet is mathematically rigorous.

To proceed we note that without knowing the precise form of the boundary discretization we know that the discretized equations can again be made to take the general form of eqn.30 which would now represent a system of $NEQC = NEQB * MXPT$ equations. In particular we shall choose to organize the component equations of the solution vector C as described in Appendix 2. Since the coefficient of $\partial C_{di}/\partial T$ is unity (see eqn.10) we can write for the concentrations at the boundary

$$\frac{\partial C_{MXPT}}{\partial T} \left(= \frac{\partial C_{NEQC - nsor + i}}{\partial T} \right) = G_{NEQC - nsor + i} \quad (40)$$

Now, since $\partial C_{MXPT} / \partial X = 0$ for all time, the derivative of this quantity with respect to time is also equal to zero. The usefulness of this fact becomes obvious if we differentiate eqn.40 with respect to X and then reverse the order of differentiation on the right-hand side for we then obtain

$$\frac{\partial}{\partial T} \left(\frac{\partial C_{MXPT}}{\partial X} \right) = \frac{\partial G_{NEQC - nsor + i}}{\partial X} = 0. \quad (41)$$

Now we can use the result in eqn.38 to express the G 's corresponding to the outlet boundary in terms of the appropriate G 's corresponding to previous grid points along the column i.e. we have

$$G_{NEQC - nsor + i} = -\frac{4G_{NEQC - nsor + i - NEQB} - G_{NEQC - nsor + i - 2 \times NEQB}}{3}. \quad (42)$$

In the computational procedure the G 's on the right hand side of eqn.42 are explicit functions of the unknown concentrations (see eqn.A2.3). The use of eqn.42 allows us to bypass the necessity of also evaluating the boundary G 's as functions of the unknown concentrations (and thus bypass the instability producing discretization) by allowing us to express them solely in terms of other G 's.

Along with the vectors $\vec{C}$ and $\vec{G}$ the components of the matrix A are given in appendix A.2.

As for the batch model eqn.30 for the column model is solved using LSODI.

SCALING AND STORAGE OPTIMIZATION

If the elements of the matrix A in eqn.30 were examined for typical "favourable" adsorption isotherms (especially at early times in the solution procedure) it would be seen that the row elements corresponding to the particle concentrations can be several orders of magnitude greater than unity which is the single row element corresponding to the free fluid concentrations. If left untreated this situation can lead to serious round-off error in the solutions determined by LSODI. Therefore, to avoid this problem in the programs, these rows of A and the corresponding components of $\vec{G}$ are scaled by dividing each element by the absolute value of the row element (in each row) of largest magnitude.

Also, since in both cases A is a banded matrix (with band-width of $2 \times nsor - 1$) it would be inefficient to store all the components since only the components within the band are non-zero. Therefore, in the programs only the band diagonals of A are stored in matrices of dimension $(2 \times nsor - 1) \times NEQB$ or $(2 \times nsor - 1) \times NEQC$.

INTERVENTIONS IN THE SOLUTION PROCEDURES

In tests of the software for both models we have found that the solution for the particle concentrations at or near the particle centre at very early times (i.e. at times too small for adsorbate from the free fluid to have diffused that far) may fluctuate slightly instead of maintaining initial values. While the size of the fluctuations is strongly influenced by the error tolerances that are user specified for LSODI negative values may appear. If these values are used in the coefficient matrix A to determine derivatives of the equilibrium isotherms (see eqn.9) a

program execution error will occur if the evaluation of a fractional power of a negative number is encountered. To avoid this absolute values of the concentrations are used in A and it is found that the concentrations soon all become positive.

With the column software it is found that very small negative values can sometimes also occur for free fluid solutions at the outlet at early times before any of the inlet concentration can reach it. We have found that this behaviour usually disappears quite quickly, however, in one simulation we found that the negative values continued to grow and spread in one of the concentrations. To prevent these small negative values from arising at all early in the solution we impose symmetry conditions at the outlet and use the central difference approximation for the second derivative in the discretization of the spatial term eqn.30 (this is similar to the discretization of eqn.18 at $R = 0$) rather than using eqn.42 in the program right from $T = 0$. This is found to keep the outlet concentrations positive; then when they reach a certain value (say 10^{-4} or so) eqn.42 is used for the boundary discretization for the remainder of the simulation.

CODE VERIFICATION

In our original unsolicited proposal we proposed to develop batch and column adsorption simulators that were based on the method of orthogonal collocation since a preliminary survey of the literature in the area seemed to indicate that this method would likely be the most computationally efficient. We had also intended to verify these simulators by reproducing results that had already been published in the literature using this method. In particular, we had intended to verify the batch simulator by reproducing the results of Liapis and Rippin (38) in which the binary adsorption of butanol-2 and t-amylalcohol by activated carbon with pore diffusion is simulated and to verify the column simulator by reproducing the simulation of Liapis and Litchfield (49) for the ternary adsorption of butanol-2, t-amylalcohol and phenol on activated carbon. However during our work on the batch simulator we found that we could not reproduce the required results and a subsequent telephone conversation with Dr. Liapis indicated that some unpublished adjustments had been used in the numerical procedure. Since these adjustments are subjectively made and we wanted a more rigorous test for the validity of our code we decided that we would consider the code to be verified if we could obtain similar results with a different numerical method. Hence a finite difference code was developed first for the batch model and then later for the column model as well. As mentioned earlier, after conducting several simulations with both methods we eventually decided to submit the finite difference simulators to EMR after approval of the Scientific Authority.

Since the collocation simulators are of secondary interest to this report we will not discuss their development except to say that discretized systems of equations of the form of eqn.30 are obtained and that LSODI is again used for the temporal integration. Also, due to oscillations in the particle concentrations absolute values of these quantities are again used in the matrix A .

We shall now present some of the verification runs made with both the collocation and finite difference codes beginning with the batch simulators. It should be noted that in all of the comparative runs that follow the inputs to LSODI that affect the accuracy (and hence the speed) of the temporal integration (such as convergence criteria etc.) are set identically for each method.

BATCH SIMULATOR VERIFICATION

For the batch simulator verification we present results obtained with the parameter values used by Liapis and Rippin in their simulation discussed above. These are:

$$\epsilon = 0.9859$$

$$\epsilon_p = 0.94$$

$$c_{01} = c_{02} = 0.0005 \text{ gm/cm}^3$$

$$D_{p1} = 7.92 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$D_{p2} = 14.64 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$K_{f1} = 4.472 \times 10^{-3} \text{ cm/sec}$$

$$K_{f2} = 4.132 \times 10^{-3} \text{ cm/sec}$$

$$r_0 = 0.05 \text{ cm} \quad (43)$$

where the subscript 1 refers to butanol-2 and the subscript 2 refers to t-amylalcohol.

The equilibrium adsorption isotherms are given by

$$C_{s1} = \frac{1.06c_{p1}^{1.217}}{c_{s01}(c_{p1}^{0.812} + 0.626c_{p2}^{0.764})} \quad (44)$$

and

$$C_{s2} = \frac{1.07c_{p2}^{1.254}}{c_{s02}(c_{p2}^{0.908} + 0.045c_{p1}^{0.634})} \quad (45)$$

The results are given in the tables below (where NRCOL represents the number of internal radial collocation points).

Table 1 - Results using orthogonal collocation plus LSODI.

t (sec)	C_{s1}		C_{s2}	
	NRCOL=5	NRCOL=10	NRCOL=5	NRCOL=10
0	1.00	1.00	1.00	1.00
600	.66	.66	.51	.51
1200	.57	.57	.40	.40
1800	.52	.52	.34	.34
2400	.48	.48	.31	.31
3000	.46	.46	.29	.29
3600	.44	.44	.28	.27
4200	.43	.43	.27	.26
4800	.42	.42	.26	.26
5400	.42	.42	.25	.25

CPU execution time on CYBER 170-835 = 28 seconds with NRCOL = 5

= 102 seconds with NRCOL = 10.

Table 2 - Results using finite differences plus LSODI.

t (sec)	C_a		C_a	
	DR=.1	DR=.05	DR=.1	DR=.05
0	1.00	1.00	1.00	1.00
600	.66	.66	.51	.51
1200	.57	.57	.40	.40
1800	.52	.51	.34	.34
2400	.48	.48	.31	.31
3000	.46	.46	.29	.29
3600	.44	.44	.27	.27
4200	.43	.43	.26	.26
4800	.42	.42	.26	.26
5400	.41	.41	.25	.25

CPU execution time on CYBER 170-835 = 47 seconds with DR = .1

= 108 seconds with DR = .05.

It should be noted that because of the forms of the equilibrium isotherms (the partial derivatives tend towards infinity as the concentrations tend towards zero) it was necessary to start the simulation off by assuming a small initial concentration in the particles (see Marcussen (36) for more discussion on this). We used a value of 10^{-13} and tests using other small values such as 10^{-4} showed no appreciable difference.

As can be seen from the tables the two batch simulators produce results that agree very well with each other and we consider both codes to be verified.

COLUMN SIMULATOR VERIFICATION

For the verification of the column simulators we present results obtained with the parameters used by Liapis and Litchfield in their simulation of the ternary adsorption of butanol-2, t-amylalcohol and phenol by activated carbon except that we shall use a smaller column length in order to reduce the computing cost. The parameter values are:

$$\varepsilon = 0.45$$

$$\varepsilon_p = 0.94$$

$$c_{01} = c_{1,ja} = 9.15 \times 10^{-4} \text{ g/cm}^3$$

$$c_{02} = c_{2,ja} = 9.12 \times 10^{-4} \text{ g/cm}^3$$

$$c_{03} = c_{3,ja} = 9.97 \times 10^{-4} \text{ g/cm}^3$$

$$D_1 = D_2 = D_3 = 0.04 \text{ cm}^2/\text{sec}$$

$$D_{p1} = 0.76 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$D_{p2} = 1.27 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$D_{p3} = 1.92 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$K_{A1} = 2.12 \times 10^{-3} \text{ cm/sec}$$

$$K_{A2} = 1.95 \times 10^{-3} \text{ cm/sec}$$

$$K_{A3} = 2.17 \times 10^{-3} \text{ cm/sec}$$

$$L = 20.5 \text{ cm}$$

$$r_0 = 0.05 \text{ cm}$$

$$V = 0.14 \text{ cm/sec} \quad (46)$$

where the subscript 1 refers to butanol-2, the subscript 2 to t-amylalcohol and the subscript 3 to phenol. The equilibrium isotherms are given by

$$C_{s1} = \frac{1.05c_{p1}^{1.134}}{c_{s01}(c_{p1}^{0.73} + 1.44c_{p2}^{0.793} + 0.53c_{p3}^{0.467})}, \quad (47)$$

$$C_{s2} = \frac{1.09c_{p2}^{1.182}}{c_{s02}(c_{p2}^{0.831} + 0.52c_{p1}^{0.884} + 0.30c_{p3}^{0.536})}, \quad (48)$$

and

$$C_{s3} = \frac{0.79c_{p3}^{0.224}}{c_{s03}(c_{p3}^{0.002} + 1.07c_{p1}^{0.286} + 0.79c_{p2}^{0.232})}. \quad (49)$$

The most crucial determiners of computing cost (other than the time to which the simulations are run) are the number of grid points to be used along the particle radius and along the column axis and these should be minimized as much as possible. To determine the grid sizes to be used along the particle radius we first ran both batch simulators to equilibrium with a few different grid sizes using the appropriate parameters of (46), a value of .9859 for the batch void fraction and the isotherms of eqns.47-49. The results showed that $NRCOL = 5$ and $DR = 1/5$ gave results that agreed sufficiently well with those obtained at higher resolutions (to two decimal places at most points in time). Figure 1 shows the results of one of these calculations. We note that the CPU execution time in this case has been obtained with the use of optimization in the compilation.

Figures 2 and 3 show the breakthrough curves obtained with collocation using $NXCOL = 8$ and $NXCOL = 10$ where $NXCOL$ is the number of internal collocation points used along the column axis. It can be seen that the unphysical overshooting and undershooting that occurs near the end of the runs is reduced with the smaller grid size but the CPU execution time is almost doubled (from 6945 to 13,605 seconds) and a smaller grid yet would still be required to further reduce or eliminate the unphysical behaviour of the outlet concentrations. Also, an inspection of the concentrations at the other axial collocation points reveals that the solution is prone to persistent oscillations along the column length. Similar behaviour in the simulation of a plug flow adsorption column with collocation has been reported by Rutzler (70).

Figures 4 and 5 show results obtained with the finite difference simulator using $DX = 1/9$ and $DX = 1/12$ with CPU execution times of 7843 and 12,744 seconds respectively. As can be seen the results are virtually indistinguishable and no unphysical behaviour is evident at the outlet. The solution at the other grid points along the column also does not exhibit the oscillatory behaviour that is found in the collocation solution.

In these column simulations both the particle and free fluid concentrations were set to an initial value of 10^{-13} and the main program was compiled using an optimization option. Lower execution times would probably be obtained if LSODI were compiled with optimization as well.

While the results of the the calculations using the column simulators do not agree as well quantitatively as in the batch case there is at least a good qualitative agreement and we consider both codes to be verified. However since we have more faith in the results of the finite difference simulator than the collocation simulator and since the latter does not appear be significantly (if at all) more computationally efficient than the latter for the cases we have tested we have chosen to submit the finite difference column simulator to EMR along with the finite difference version of the batch simulator.

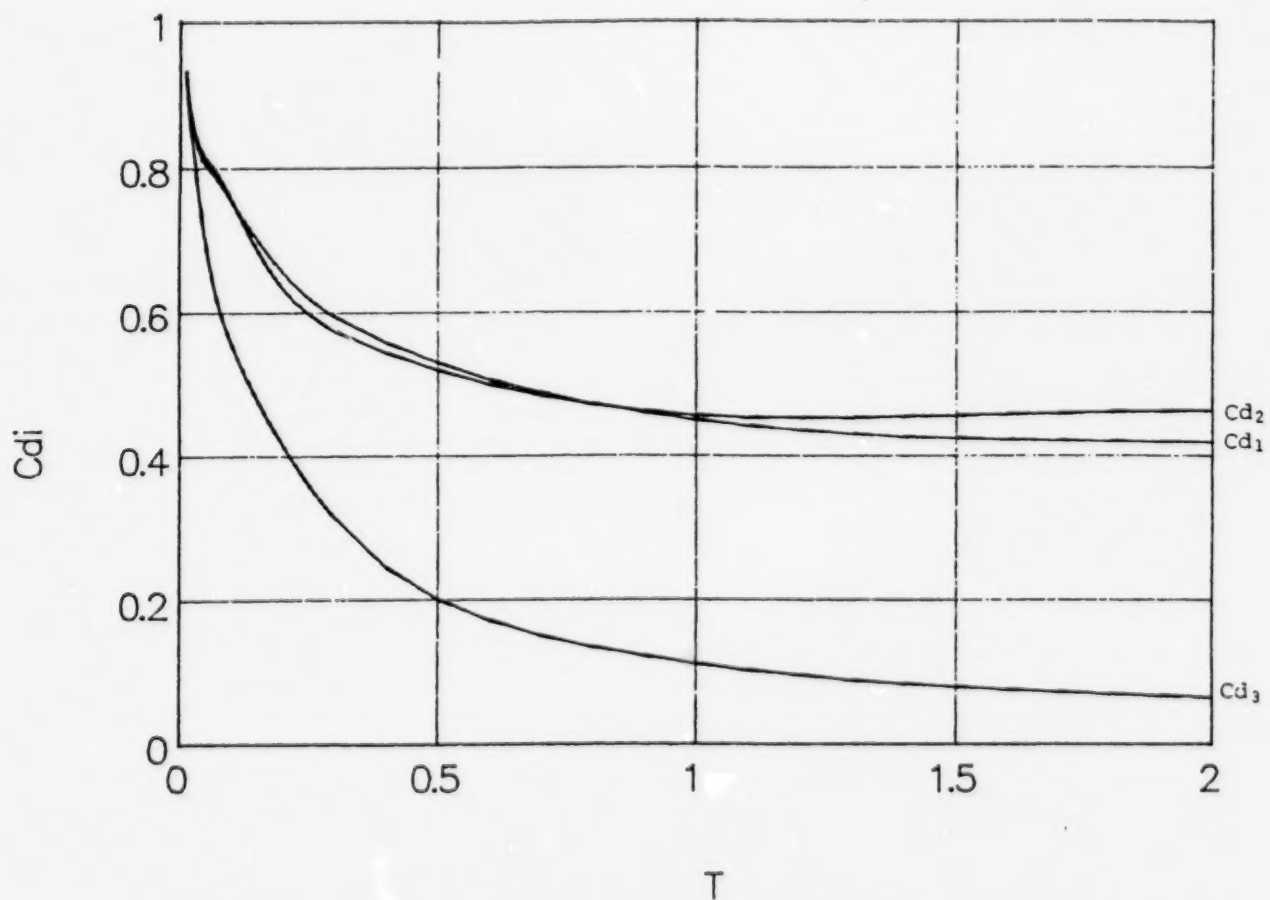


FIGURE 1. CONCENTRATION VS. TIME FINITE DIFFERENCE SOLUTION
DR = 1/5 CPU = 47 sec.

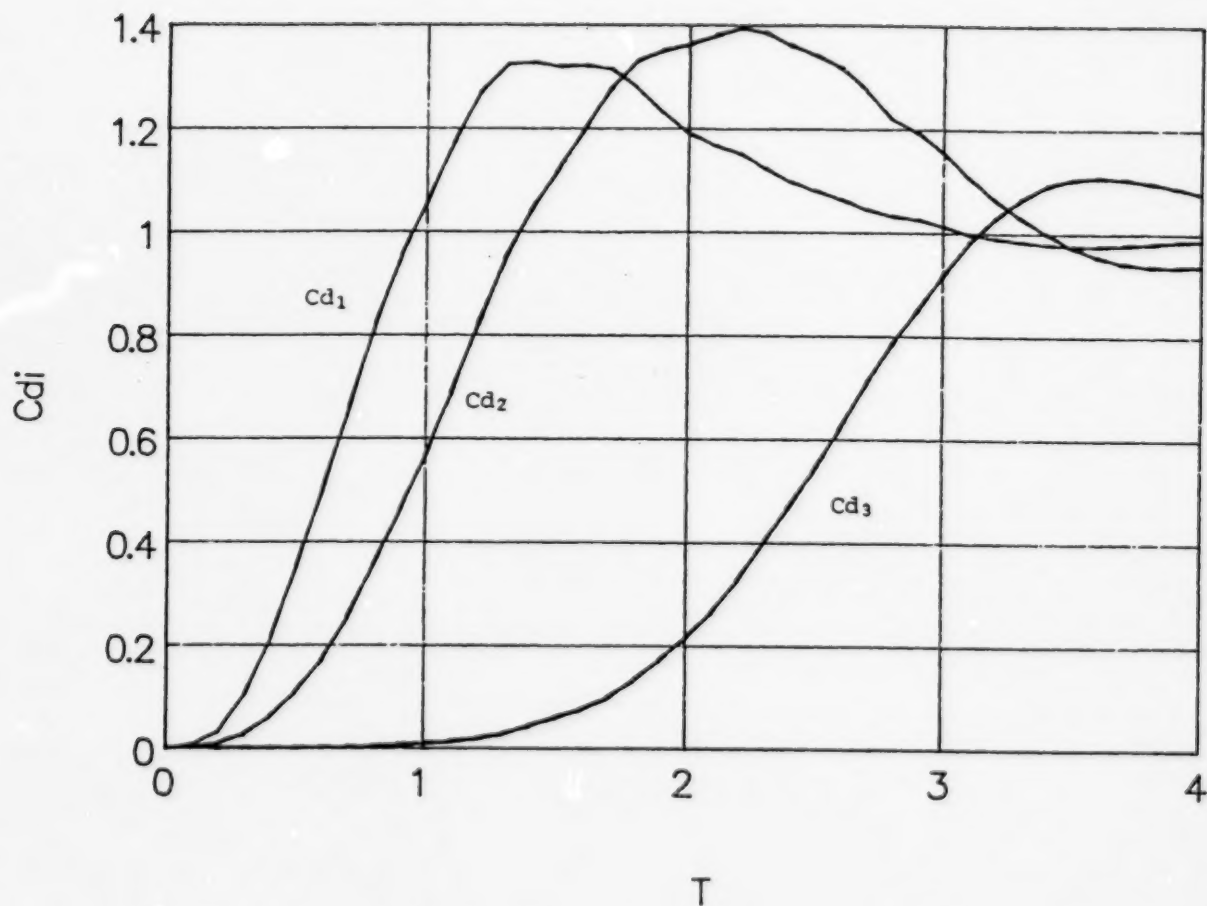


FIGURE 2. BREAKTHROUGH CURVES $L = 20.5$ cm.
COLLOCATION SOLUTION $NRCOL = 5$, $NXCOL = 8$, CPU = 6945 sec.

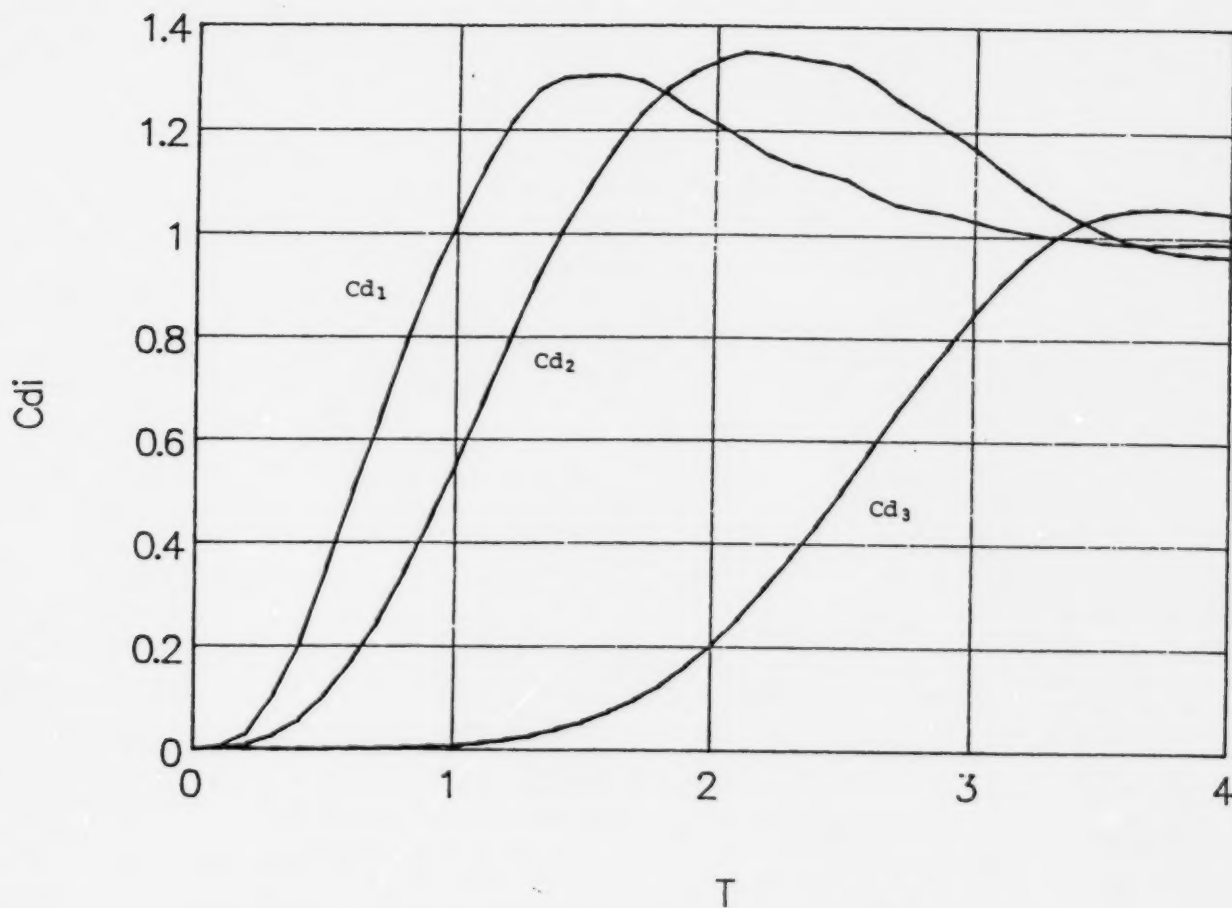


FIGURE 3. BREAKTHROUGH CURVES $L = 20.5$ cm.
COLLOCATION SOLUTION $NRCOL = 5$, $NXCOL = 10$, CPU = 13,605 sec.

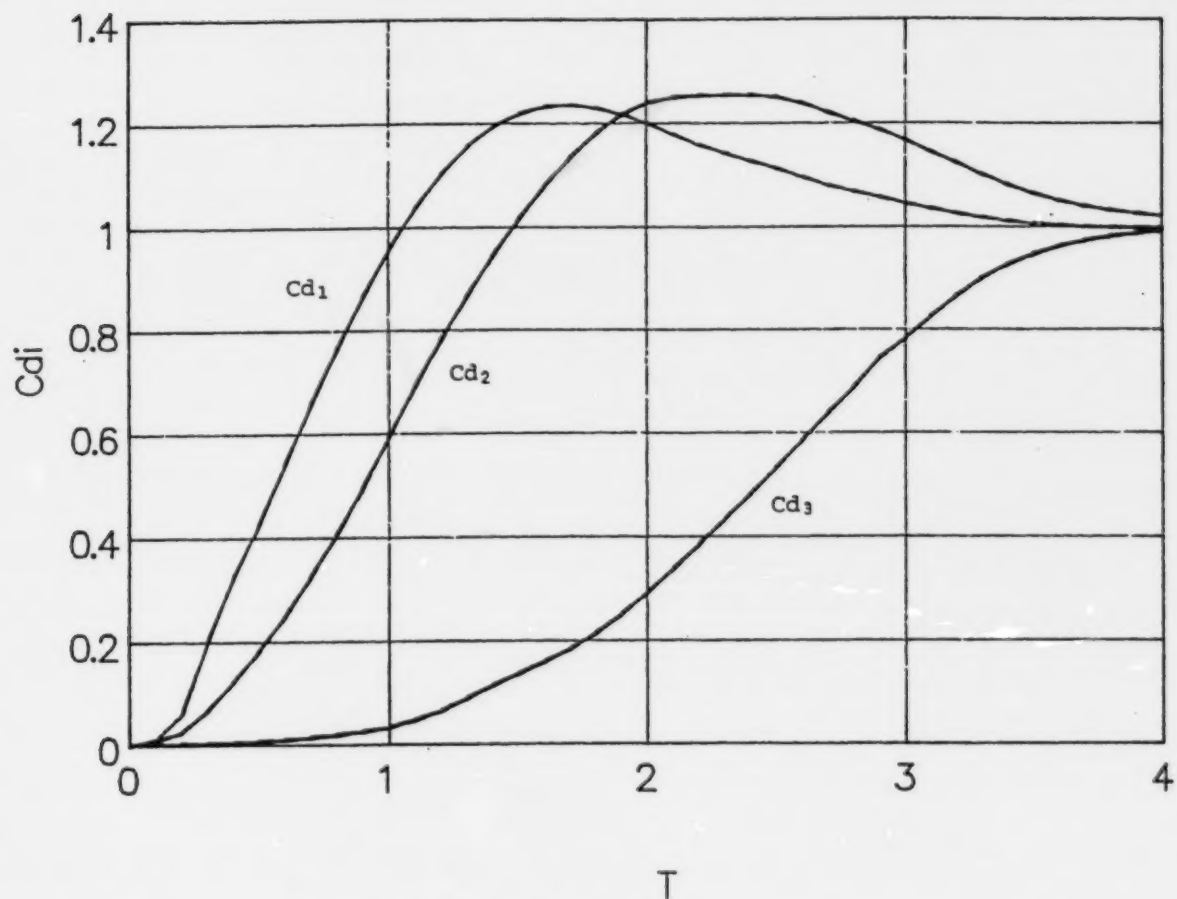


FIGURE 4. BREAKTHROUGH CURVES $L = 20.5$ cm.
FINITE DIFFERENCE SOLUTION $DR = 1/5$, $DX = 1/9$, CPU = 7843 sec.

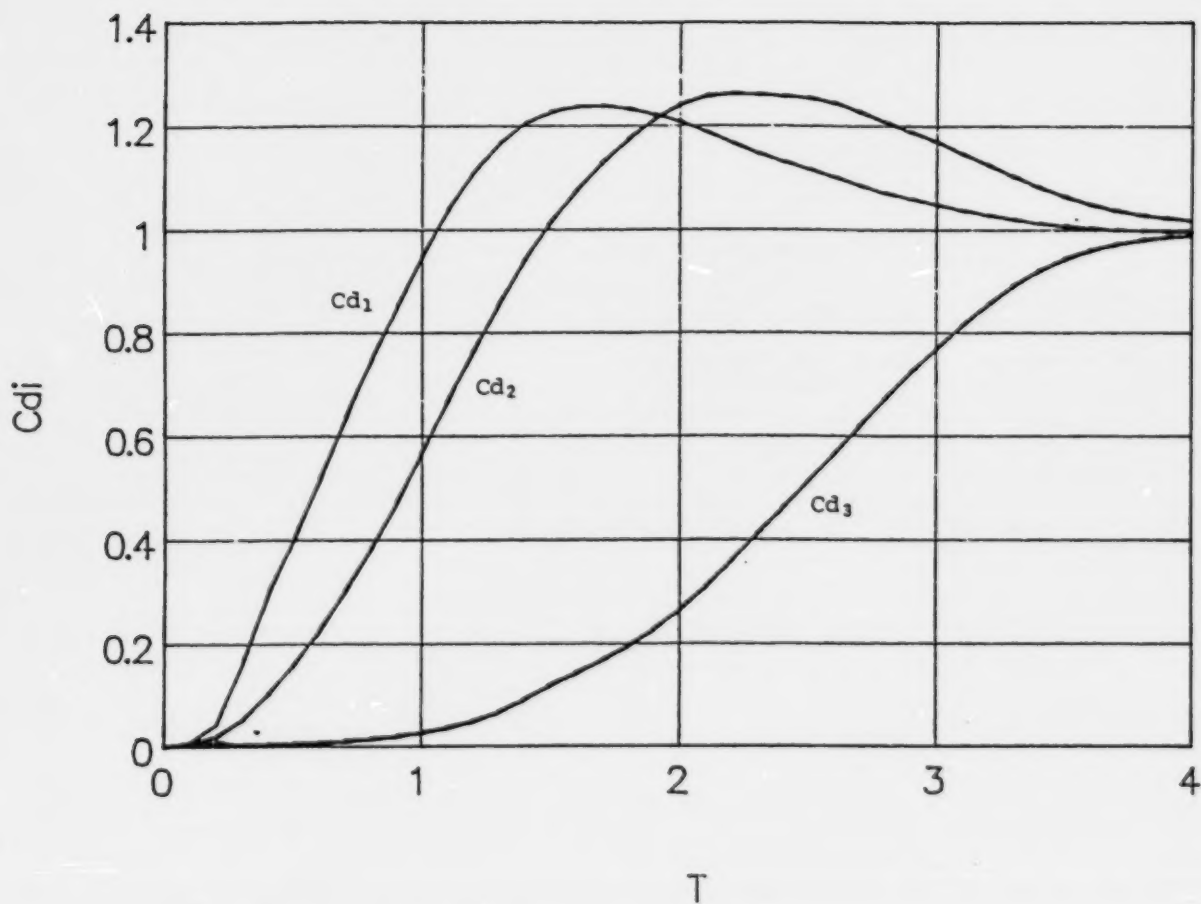


FIGURE 5. BREAKTHROUGH CURVES $L = 20.5$ cm.
FINITE DIFFERENCE SOLUTION $DR = 1/5$, $DX = 1/12$, CPU = 12,744 sec.

INSTRUCTIONS ON THE USE OF THE SIMULATORS

The new user should read through the documentation of the main programs (appendices A.3, A.6) as well as the LSODI manual for a listing of the program parameters and required inputs. The majority of the inputs that are required are values of physical parameters such as the particle radius and void fraction which are entered into a data input file for each simulator. The other inputs required are formulae for the partial derivatives of the equilibrium isotherm(s) which are coded in a user supplied SUBROUTINE DFDC which is identical for each simulator except for COMMON and DIMENSION statements. Beyond these the main programs contain a number of values such as those relating to grid size(s) and error tolerances for LSODI that can be reset as needed.

We note that correlations for the batch mass transfer coefficients are given by Calderbank and Jones (71) and Harriott (72) while correlations for the column mass transfer coefficients are given by Wilson and Geankoplis (73), Mandelbaum and Boehm (74) and Wilke and Hougen (75) and correlations for the axial diffusion coefficients are given by Liles and Geankoplis (76). Also, if the actual adsorbent pellets are not spherical formulae required for representing them as equivalent spheres are given in Bird et al. (77).

Examples of appropriate data input files for the batch and column simulators are given in the appendices A.4 and A.7 which contain the parameter values used in the verification runs discussed previously. Sample output from these runs are given in A.5 and A.8.

We note that a non-linear regression routine such as the SAS routine PROC NLIN is generally needed to obtain a functional fit to the data obtained by preliminary experiments performed to determine equilibrium isotherms. Since the first derivatives of these isotherms are used in the program calculations it is important that these isotherms do not exhibit unphysical behaviour over the concentration ranges of interest. For example, if the isotherms should be favourable (i.e. have positive and monotonically decreasing slopes) then a data fit should not have oscillatory behaviour in the slopes since this could sooner or later cause convergence problems in the programs. Thus in choosing a model (functional form) with which to fit the data it may be necessary to pick one that may not fit the data as well as another but has more realistic behaviour in its derivatives.

Recall now that the primary purpose of the batch simulator in the context of this report is to determine an estimate of the macropore diffusion coefficient for each adsorbate for later use with the column simulator. To do this one could start by choosing a grid size of say $DR=.1$ ($NRPT=11$) and an absolute error tolerances for LSODI of $ATOL=10^{-4}$ (we have found that a relative error tolerance of $RTOL=10^{-4}$ is generally sufficient when the option $ITOL=1$ is used) and then running the simulator with values of the diffusivities that are large enough to allow attainment of equilibrium (i.e. concentration at the centre of the particles equal to the bulk fluid concentration) within the time determined by the experimental data. One should then experiment with smaller grid sizes and values of $ATOL$ to ensure that the numerical solution is converging adequately. In general smaller grid sizes should be necessary as the Sherwood number increases.

At this stage it may be found that the bulk equilibrium concentrations are higher or lower than the experimental results. This is most easily remedied by adjusting the batch void fraction which has a great effect in determining the equilibrium concentrations but may not be input initially with adequate precision (for useful information on the effects of all the parameters see the parametric sensitivity study of Mansour et al. (78) on batch multicomponent adsorption). Once the predicted equilibrium concentrations have been adequately matched to the experimental results the diffusivities can be reduced to match the experimental concentration vs. time curves as much as possible over the entire time domain.

When satisfactory matching has been obtained a few more runs with different grid sizes and values of ATOL should be done to ensure adequate convergence.

The column simulator can then be run using the diffusivity estimates determined with the batch simulator. To start it will be necessary to choose an axial grid size DX , a radial grid size DR and a value of ATOL and then (as in the case of the batch simulator) experiment with different values to ensure adequate convergence. Because the column simulator will require significantly more computer time than the batch simulator is particularly worthwhile to determine the largest grid sizes that can satisfactorily be used. To save computer time we recommend that these initial simulations only be run to a fraction of the total experimental simulation time, say only till significant breakthrough should be evident. It can be expected that the higher the Peclet number the smaller the axial grid size that will be required. Alternatively one could first determine the largest satisfactory size of DR by using the values of the column mass transfer coefficients with the batch simulator and then experimenting with the column simulator to determine DX and ATOL. We also note that in our experience we have found that the value of ATOL required to obtain adequate convergence with the column simulator is usually larger than is required with the batch simulator (10^{-6} is almost always sufficient).

When satisfactory agreement between the simulation and experimental data has been attained one can then conduct computer experiments with different input parameters such as the column length and initial concentrations to predict the breakthrough curves rather than perform the experiments themselves. Then, if an optimum adsorber configuration is being sought, physical experiments need only be done in the parameter ranges that are indicated by the simulation results as being optimum to confirm the computer predictions. Of course care must be taken in the computer experiments to ensure that if the parameter changes increase the Sherwood number and/or the Peclet number that the grid sizes are decreased appropriately. As well, concentration ranges outside of those used in determining the equilibrium isotherms should be avoided.

If it is found that reasonable agreement between the simulator results and the experimental data is not obtained one should first re-examine the input data. One might try different correlations for the batch and column film mass transfer coefficients and/or check the differentiation of the isotherms in SUBROUTINE DFDC. If no errors or unreasonable coefficient values are found then it must be concluded that the macropore diffusion model is inadequate for the system at hand and there is no use in conducting any computer experiments. One should be especially aware of the fact that as the size of the adsorbent pellet is decreased that micropore diffusion resistance becomes more important and the macropore diffusion model is less likely to be adequate (see for example Biswas et al. (79) for discussion on this).

Finally, we note that the column model can be used with pulsed concentration levels in the feedstream by assigning the appropriate time dependence to the vector CIN in SUBROUTINE RES.

TEST APPLICATION TO ORGANIC ADSORPTION ON ZEOLITE Y

To test the application of the simulators to the adsorption of organic compounds on zeolites EMR has supplied experimental data and input parameters for the single component adsorption of ethyl pyridine, the binary adsorption of ethyl pyridine and indole, and the tertiary adsorption of ethyl pyridine, indole and quinoline on zeolite Y pellets (all with toluene used as the solvent).

The parameters given for the single component case are:

$$\epsilon = 0.95$$

$$\epsilon_p = 0.5$$

$$c_{01} = 0.0178 \text{ gm/cm}^3$$

$$K_{f1} = 0.0134 \text{ cm/sec}$$

$$r_0 = 0.099 \text{ cm} \quad (50)$$

and the best fit that we could obtain from the experimental data for the determination of the equilibrium isotherm is given by

$$C_{s1} = \frac{.998c_{p1}^{2.84}}{c_{s01}} \quad (51)$$

In order to match the predicted external fluid concentration at equilibrium to the experimental value we found it necessary to adjust the batch void fraction to $\epsilon = .9654$. Then we found that the best matching of the experimental and predicted concentration vs. time curves was given by the value $D_{p1} = 2.3 \times 10^{-4}$ for the macropore diffusivity of ethyl pyridine. A comparison of the experimental and predicted data using these values is given in Table 3 below.

Table 3 - Experimental and best matching simulation results for the batch adsorption of ethyl pyridine on zeolite Y.

t (min)	C_{s1} - experiment	C_{s1} - predicted
0	1.00	1.00
15	.84	.83
30	.70	.78
60	.62	.71
90	.57	.67
120	.55	.64
150	.53	.61
200	.51	.58
300	.50	.54
400	.49	.51
500	.48	.50
600	.48	.49
700	.48	.48
800	.48	.48

Since the predicted values differ from the experimental values by as much as 18% we conclude that the agreement is not particularly good. We will examine possible reasons for this lack of agreement shortly but first we shall present experimental and simulation results for the column adsorption of ethyl pyridine using the predicted value of the diffusivity obtained with the batch simulator.

The values of the parameters used to obtain the results given in Table 4 below are:

$$\varepsilon = 0.4$$

$$\varepsilon_p = 0.5$$

$$c_{01} = c_{1,2A} = 0.0178 \text{ g/cm}^3$$

$$D_1 = 0.0138 \text{ cm}^2/\text{sec}$$

$$D_{p1} = 2.3 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$K_{f1} = 1.42 \times 10^{-3} \text{ cm/sec}$$

$$L = 13.0 \text{ cm}$$

$$r_0 = 0.099 \text{ cm}$$

$$V = 0.14 \text{ cm/sec.} \quad (52)$$

Table 4 - Experimental and predicted results for the column adsorption of ethyl pyridine on zeolite Y.

t (min)	C _{at} - experiment	C _{at} - predicted
0	.00	.00
8.70	.00	.00
17.39	.00	.07
26.09	.01	.50
34.78	.04	.70
43.48	.08	.70
52.17	.13	.71
60.87	.18	.71
69.57	.24	.72
78.26	.30	.74
86.96	.37	.75
95.65	.43	.77
104.35	.49	.78
113.04	.55	.79
121.74	.61	.81
130.44	.66	.83
139.13	.71	.84
147.83	.77	.85
156.52	.81	.85
165.22	.86	.86
173.91	.90	.86
182.61	.93	.87
191.30	.96	.87
200.00	.98	.88
208.70	1.0	.88

As is readily apparent the results do not agree at all well since the predicted breakthrough occurs much too early. We performed a number of additional runs trying different values of the diffusivity to improve the matching and found the best result using $D_{p1} = 4.8 \times 10^{-5}$. With this value the agreement is very good for the first hour but thereafter the predicted breakthrough occurs much quicker than the experimental results indicate. We shall now suggest some possible reasons for the lack of agreement between the experimental and predicted values for both the batch and column cases.

To begin it will be useful to consider the work of Santacesaria et al. (39,56) who have successfully simulated the batch and column adsorption of as many as four organic solutes on zeolite Y (exchanged with potassium) using a macropore diffusion model. In fact the batch model that they employ is identical to the model used in this report except for a minor change in the boundary condition involving the concentration at the particle surface. The column model that they use is a "lumped" version of the model that we use. The advantage of using the lumping procedure lies in the fact that the number of spatial dimensions in the model is reduced by one since the average particle concentration as a function of the axial position is solved for rather than the particle concentration proper which is a function of both radial distance within the particle as well as axial positions and thus computer time is significantly reduced. However a potentially serious drawback to this procedure is the fact that the averaging process leads to the definition of mass transfer coefficients which are no longer constant but are time-varying.

Santacesaria et al. analyzed the time dependence of these coefficients for their particular system and were able to justify the use of some average value. However, as they point out, this may not always be possible with other systems. Hence, to keep the simulators as generally applicable as possible we opted not to use the lumping procedure. Nevertheless we wish to stress the fact that if the lumped model gives good results with a system then the un-lumped model should give results that are as good or better since the former is only an approximation to the latter.

We refer to the work of Santacesaria et al. here primarily because it immediately suggests two factors that may contribute to the lack of agreement between the experimental and predicted results presented above. Firstly, they give a value of $\epsilon_p = .2$ for the zeolite Y pellets they use which is substantially different from the value of $\epsilon_p = .5$ that we have been given which suggests that the particle void fraction should be checked. Secondly, they employ a thermostatic bath to ensure that the column is maintained isothermal and since the feedstream concentrations that they use are of the same order of magnitude as that used to obtain the experimental results above (with no thermostatic bath) it suggests that perhaps the assumption of isothermality is violated at this level of concentration and that a significantly lower concentration should be used.

As well, an analytic and/or experimental investigation of the relative importance of micropore diffusion with the adsorbents and pellet size used should be carried out to make certain that the macropore diffusion is still rate limiting. In addition, it would probably be worthwhile to recalculate those input parameters derived from correlations with the correlations employed by Santacesaria et al. to check for major differences.

Due to time and budget constraints we were not able to collaborate with EMR to investigate these issues further. Also, since we considered it to be unreasonable to expect to successfully simulate the multicomponent cases without being able to simulate the single component case we did not spend much time attempting to do so (with little success).

CONCLUSIONS

We have developed computer codes for the simulation of both batch and column multicomponent adsorption based on a macropore diffusion model. The codes have been verified by obtaining similar results with the use of two different numerical techniques. A test application to the adsorption of organic compounds on zeolite was unsuccessful, however, we have pointed out some possible reasons for this that require further investigation. We have noted previously published work that clearly indicates great promise for the simulation of this type of system using the macropore diffusion model. It has been observed that both the collocation and finite difference methods were suitable for the batch model but that the finite difference method was preferable to the collocation method in the case of the column model. When the necessary experience with the use of these simulators has been gained they should prove to be useful to the scientists at EMR who are also studying systems of this type.

SUGGESTIONS FOR FURTHER WORK

To extend this work there are many avenues that could be considered of which we will mention only some of the most obvious. For example, a parametric sensitivity study for the column model could be conducted as has already been done for the batch model by Mansour et al. (78). Or, since the determination of the multicomponent equilibrium isotherms can still require a significant amount of experimental work, a study could be done on the feasibility of constructing these from single or perhaps binary component isotherms for organic adsorption on zeolites as has been done for organic adsorption on carbon (see Sheindorf et al. (55)). Alternatively, the possibility of incorporating IAS theory into the models to estimate these isotherms could be studied.

Also, the feasibility of extending the models to include non-isothermality and/or micropore diffusion could be investigated.

NOTATION

A matrix of dimension $NEQB \times NEQB$ or $NEQC \times NEQC$

A_0 external surface area of the spherical particles, cm^2

$\vec{c}$ vector of length $NEQB$ or $NEQC$

C_{di} dimensionless concentration of solute i in free fluid phase, c_{di}/c_{0i}

where c_{di} = concentration of solute i in free fluid phase, g/cm^3

c_{0i} = initial inlet concentration of solute at $x < 0$, or initial batch fluid concentration, g/cm^3

$C_{i,in}$ dimensionless inlet concentration of solute i , $c_{i,in}/c_{0i}$

where $c_{i,in}$ = inlet concentration, g/cm^3

C_{pi} dimensionless concentration of solute i in pore fluid phase, c_{pi}/c_{0i}

where c_{pi} = concentration of solute i in pore fluid phase, g/cm^3

C_{si} dimensionless concentration of solute i in solid (adsorbed) phase, c_{si}/c_{0i}

where c_{si} = concentration of solute i in solid phase (per unit volume of particles), g/cm^3

c_{s0i}^* value of c_{si} in equilibrium with c_{0i} , g/cm^3

D_{Li} axial diffusivity of solute i , cm^2/sec

D_{pi} effective diffusivity of solute i in pore fluid, cm^2/sec

$\vec{g}$ vector of length $NEQB$ or $NEQC$

K_f film mass transfer coefficient of solute i , cm/sec

L length of column, cm

$MXPT$ number of finite difference grid points along column axis

$NEQB$ number of equations in discretized batch model, $(NRPT + 1) \times nsor$

$NEQC$ number of equations in discretized column model, $(NRPT + 1) \times nsor \times MXPT$

$NRCOL$ number of internal collocation points along particle radius

$NRPT$ number of finite difference grid points along particle radius

$NXCOL$ number of internal collocation points along column axis

$nsor$ number of adsorbed solute species

Pe_i Peclet number, $LV/\epsilon D_{Li}$

R dimensionless radial coordinate, r/r_0

where r = radial distance in particle, cm

r_0 = radius of particle, cm

R_n label of n th radial grid point in particle

Sh_{pi} modified particle Sherwood number, $2r_0K_f/\epsilon_p D_{pi}$

T dimensionless time, tD_{pi}/A_0

where t = time from start of adsorption process, sec

V superficial fluid velocity, cm/sec

X dimensionless bed length coordinate, x/L
where x = distance measured from column inlet, cm

X_m label of m th axial grid point along column

Greek symbols

ϵ void fraction in the bed or batch system

ϵ_p void fraction in the particles

APPENDIX A.1 DISCRETIZED BATCH MODEL EQUATIONS

In this appendix we give the components of the system of discretized equations

$$A \frac{\partial \vec{C}}{\partial T} = \vec{G}$$

for the batch model.

The matrix A of dimension $NEQB \times NEQB$ can be written as a block diagonal matrix in terms of $NRPT + 1$ sub-matrices of dimension $nsor \times nsor$ i.e.

$$A = \begin{pmatrix} A_1 & 0 & . & . & . & . \\ 0 & A_2 & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & A_{NRPT} & 0 \\ . & . & . & . & 0 & A_{NRPT+1} \end{pmatrix}. \quad (A.1.1)$$

Each matrix A_n where $1 \leq n \leq NRPT$ has the component form

$$A_n = \frac{1}{C_{01}} \begin{pmatrix} \epsilon_p + \frac{\partial f_1}{\partial C_{p1n}} & \frac{\partial f_1}{\partial C_{p2n}} & . & . & . & \frac{\partial f_1}{\partial C_{pnsor n}} \\ \frac{\partial f_2}{\partial C_{p1n}} & \epsilon_p + \frac{\partial f_2}{\partial C_{p2n}} & . & . & . & \frac{\partial f_2}{\partial C_{pnsor n}} \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ \frac{\partial f_{nsor}}{\partial C_{p1n}} & . & . & . & \frac{\partial f_{nsor}}{\partial C_{pnsor-1n}} & \epsilon_p + \frac{\partial f_{nsor}}{\partial C_{pnsor n}} \end{pmatrix} \quad (A.1.2)$$

The matrix A_{NRPT+1} is simply an identity matrix (i.e. unit elements on the main diagonal and zero elements everywhere else).

The vector $\vec{C}$ has the following form

$$\vec{C} = \begin{pmatrix} C_{p11} \\ C_{p21} \\ \vdots \\ C_{pNRPT1} \\ C_{p12} \\ C_{p22} \\ \vdots \\ C_{pNRPT2} \\ \vdots \\ C_{p1NRPT} \\ C_{p2NRPT} \\ \vdots \\ C_{pNRPTNRPT} \\ C_{d1} \\ C_{d2} \\ \vdots \\ C_{dNRPT} \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_{NRPT} \\ C_{NRPT+1} \\ C_{NRPT+2} \\ \vdots \\ C_{2 \times NRPT} \\ \vdots \\ C_{(NRPT-1) \times NRPT+1} \\ C_{(NRPT-1) \times NRPT+2} \\ \vdots \\ C_{NRPT \times NRPT} \\ C_{NEQB - NRPT} \\ C_{NEQB - NRPT+1} \\ \vdots \\ C_{NEQB} \end{pmatrix} \quad (A.1.3)$$

As can be seen from eqn.A.1.3 the C 's correspond to the C_p 's through the rule $C_{i - NRPT \times (n-1)} = C_{pi_n}$ and the C 's correspond to the C_d 's through the rule $C_{i + NEQB} = C_{di}$.

The vector $\vec{G}$ can be written in terms of $NRPT + 1$ sub-vectors of length $NRPT$ as

$$\vec{G} = \begin{pmatrix} \vec{G}_1 \\ \vec{G}_2 \\ \vdots \\ \vdots \\ \vec{G}_{NRPT} \\ \vec{G}_{NRPT+1} \end{pmatrix} \quad (A.1.4)$$

where the components of $\vec{G}$, denoted by G_{ii} , are given by

$$G_{1i} = 6CF2_i \left(\frac{C_{i+NSOR} - C_i}{(DR)^2} \right) \quad (A.1.5)$$

and the ordering is understood to be from top to bottom with increasing i ($1 \leq i \leq NSOR$) and

$$CF2_i = \frac{4\pi\epsilon_p D_{p1} C_{0i}}{D_{p1} C_{01}}. \quad (A.1.6)$$

The components of the vectors $\vec{G}_n$ for $1 < n < NRPT$ are given by

$$\begin{aligned} G_{ni} = CF2_i & \left(C_{II+NSOR} \left(\frac{1}{(DR)^2} + \frac{1}{R_n DR} \right) - C_{II} \left(\frac{2}{(DR)^2} \right) \right. \\ & \left. + C_{II-NSOR} \left(\frac{1}{(DR)^2} - \frac{1}{R_n DR} \right) \right) \end{aligned} \quad (A.1.7)$$

where $II = i + NSOR \times (n - 1)$. For G_{NRPT} , we have

$$\begin{aligned} G_{NRPTi} = CF2_i & \left(-2Sh2_i C_{II} \left(1 + \frac{1}{DR} + \frac{1}{Sh2_i (DR)^2} \right) + C_{II-NSOR} \left(\frac{2}{(DR)^2} \right) \right. \\ & \left. + 2Sh2_i C_{i+NEQBM} \left(1 + \frac{1}{DR} \right) \right). \end{aligned} \quad (A.1.8)$$

where $Sh2_i = Sh_i/2$ and $NEQBM = NEQB - NSOR$.

Finally for $\vec{G}_{(NRPT+1)}$, we have

$$G_{(NRPT+1)i} = CF1_i (C_{i+NEQBM} - C_{i+NEQBM-NSOR}) \quad (A.1.9)$$

where

$$CF1_i = \frac{\epsilon - 1}{\epsilon} \frac{A_0}{D_{p1} r_0} \frac{3}{K_\beta}. \quad (A.1.10)$$

APPENDIX A.2 DISCRETIZED COLUMN MODEL EQUATIONS

In this appendix we give the components of the system of discretized equations

$$A \frac{\partial \vec{C}}{\partial T} = \vec{G}$$

for the column model. Since the structure of the column system is similar to that of the batch system being repeated at each axial grid point one should be thoroughly familiar with the structure of the batch system given in the previous appendix.

In this case the matrix A is of dimension $NEQC \times NEQC$ and can be written as a block diagonal matrix in terms of $MXPT$ sub-matrices each of dimension $NEQB \times NEQB$ i.e.

$$A = \begin{pmatrix} A_1 & 0 & \cdot & \cdot & \cdot & \cdot \\ 0 & A_2 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & A_{MXPT-1} & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & A_{MXPT} \end{pmatrix} \quad (A.2.1)$$

Each of the sub-matrices A_m where $1 \leq m \leq MXPT$ has exactly the same form as that given by eqn.A.1.1 for the batch model. However, for this case the C_p 's of the components given by eqn.A.1.2 are subscripted by m as well.

The vector $\vec{C}$ in this case is structured as $MXPT$ repetitions of the form given in eqn.A.1.3. with the rules $C_{i + NEQB \times (m-1) + NEQB \times (m-1)} = C_{pi,m}$ and $C_{i + NEQBM + NEQB \times (m-1)} = C_{di,m}$.

Similarly the vector $\vec{G}$ consists of $MXPT$ repetitions of the form given in eqn.A.1.4. Except for the first repetition which accounts for the inlet boundary condition and the last which accounts for the outlet condition eqn.A.1.9 is replaced with

$$G_{(NRPT+1)_m} = CF1_i(C_{II} - C_{II-NEQB}) + CF3_i \left(\frac{C_{II+NEQB} - 2C_{II} + C_{II-NEQB}}{Pe_i(DX)^2} - \frac{C_{II} - C_{II-NEQB}}{DX} \right) \quad (A.2.2)$$

where $II = i + NEQBM + NEQB \times (m-1)$. For the first repetition we have

$$G_{(NRPT+1)_1} = CF1_i(C_{II} - C_{II-NEQB}) + CF3_i \left(2 \frac{C_{II+NEQB} - C_{II}(1 + DX + Pe_i) + (DX)Pe_i c_{i,jn}/c_{0i}}{Pe_i(DX)^2} - Pe_i(C_{II} - c_{i,jn}/c_{0i}) \right) \quad (A.2.3)$$

while for the last we have

$$G_{(NRPT+1)MXPT} = G_{NEQC - Nor + i}$$

$$= \frac{4G_{NEQC - Nor + i - NEQB} - G_{NEQC - Nor + i - (2 \times NEQB)}}{3} \quad (A.2.4)$$

except for small times (as explained in the section "INTERVENTIONS IN THE SOLUTION PROCEDURES") when we have

$$G_{(NRPT+1)MXPT} = CF1_i(C_{II} - C_{II - Nor}) + 2CF3_i \frac{C_{II - NEQB} - C_{II}}{Pe_i(DX)^2}. \quad (A.2.5)$$

APPENDIX A.3 - BATCH SIMULATOR CODE

```

PROGRAM BATCH (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C THIS IS THE MAIN PROGRAM FOR THE BATCH SIMULATOR. IT HAS BEEN
C WRITTEN FOR USE WITH LSODI (LIVERMORE SOLVER FOR ORDINARY
C DIFFERENTIAL EQUATIONS (IMPLICIT FORM) MARCH 30, 1987 VERSION)
C WHICH CAN BE USED TO SOLVE INITIAL VALUE PROBLEMS FOR LINEARLY
C IMPLICIT FIRST ORDER DIFFERENTIAL EQUATIONS OF THE GENERAL
C FORM  $A(T,Y)*DY/DT=G(T,Y)$ .
C
C MOST OF THE PROGRAM VARIABLES ARE DEFINED IN THE ACCOMPANYING
C REPORT OR THE LSODI MANUAL. THOSE FEW THAT ARE NOT AND ARE NOT
C OBVIOUS ARE DESCRIBED AS THEY ARE DEFINED IN THE PROGRAM.
C
C NOTE THAT  $NEQB=NSOR*(NRPT+1)$ 
C LRW=DIMENSION OF VECTOR RWORK
C      =.GE.22+17*NEQB+(2*ML+MU)*NEQB FOR MF=15
C LIW=DIMENSION OF VECTOR IWORK
C      =.GE.20+NEQB
C
C PARAMETER (NSOR=2,NRPT=6,NEQB=14)
C EXTERNAL RES,ADDA
C DIMENSION C(NEQB),CDOTI(NEQB),RWORK(9000),IWORK(900)
C COMMON /BLK1/ CF1(5),CF2(5),DP(5),SH2(5),C0(5),EP,DR,DR2
C COMMON /BLK2/ AD(5,50),G(50),RPT(50)
C COMMON /BLK3/ NEQBM,NRPTM
C REAL KF(5)
C
C PI = 3.1415926535897
C NEQBM = NEQB-NSOR
C NRPTM = NRPT-1
C
C READ PARTICLE RADIUS, VOID FRACTION AND BED VOID FRACTION
C READ (5,*) R0,EP,EB
C A0 = 4*PI*R0**2
C
C READ DIFFUSIVITIES, FILM MASS TRANSFER COEFFICIENTS AND
C INITIAL DIMENSIONAL BULK CONCENTRATIONS
C READ (5,*) (DP(L),L=1,NSOR)
C READ (5,*) (KF(L),L=1,NSOR)
C READ (5,*) (C0(L),L=1,NSOR)
C
C READ TOTAL SIMULATION TIME IN SECONDS AND NUMBER OF EQUALLY
C SPACED TIME STEPS AT WHICH OUTPUT IS DESIRED
C READ (5,*) TSEC,NTSTEPS
C
C TMAX = TSEC*DP(1)/A0
C DT = TMAX/NTSTEPS
C TMAX IS THE NON-DIMENSIONAL TIME LENGTH OF THE SIMULATION
C
C DEFINE SOME CONVENIENT COEFFICIENTS
C DO 10 L = 1, NSOR
C CF1(L) = (EB-1.)*KF(L)*3*A0/(EB*DP(1)*R0)
C CF2(L) = 4*PI*EP*DP(L)*C0(L)/(DP(1)*C0(1))
C SH2(L) = 2*R0*KF(L)/(EP*DP(L))
10 CONTINUE
C
C PRINT OUT INPUT PARAMETERS AND THEN REDEFINE SH2
C WRITE (6,20) NSOR
20 FORMAT (2X,'NUMBER OF SORBENTS = ',I2,/)

```

```

WRITE (6,30)
30  FORMAT (2X,'PARTICLE DIFFUSIVITIES',2X,'FILM COEFFICIENTS',2X,'INI
    *TIAL BULK FLUID CONC.(G/CM**3)',2X,'SHERWOOD NUMBER',//)
C
DO 40 L = 1, NSOR
WRITE (6,50) DP(L),KF(L),C0(L),SH2(L)
SH2(L) = SH2(L)/2.
40  CONTINUE
50  FORMAT (6X,E12.6,11X,E12.6,13X,E12.6,15X,E12.6//)
C
WRITE (6,60) R0,A0,EP,EB
60  FORMAT (/2X,'R0 = ',F8.5,2X,'A0 = ',F8.5,2X,'EP = ',F8.5,2X,'EB =
    * ',F8.5//)
C
C  SET RADIAL GRID SIZE AND RADIAL GRID POINTS
DR = 1/FLOAT(NRPTM)
DR2 = DR*DR
DO 70 N = 1, NRPT
RPT(N) = (N-1)*DR
70  CONTINUE
C
C  SET INITIAL DIMENSIONLESS PARTICLE AND FREE FLUID CONCENTRATIONS
DO 80 I = 1, NSOR
DO 80 J = 1, NRPT
JJ = I+NSOR*(J-1)
C(JJ) = 1.E-13
80  CONTINUE
DO 90 I = 1, NSOR
C(NEQBM+I) = 1.
90  CONTINUE
C
C  SET INPUTS FOR LSODI - SEE LSODI MANUAL
NTIM = NTSTEPS+1
ITASK = 1
ML = NSOR-1
MU = NSOR-1
IWORK(1) = ML
IWORK(2) = MU
MF = 15
ISTATE = 0
IOPT = 1
RWORK(5) = 0.0
RWORK(6) = 0.0
RWORK(7) = 0.0
RWORK(8) = 0.0
RWORK(9) = 0.0
RWORK(10) = 0.0
IWORK(5) = 0
IWORK(6) = 600
IWORK(7) = 0
IWORK(8) = 0
IWORK(9) = 0
IWORK(10) = 0
LRW = 9000
LIW = 900
RTOL = 1.E-04
ATOL = 1.E-06
ITOL = 1
T = 0.
TOUT = T
C

```

```

      WRITE (6,100) DR,RTOL,ATOL
100  FORMAT (/2X,'DR = ',F6.3,2X,'RTOL = ',E10.5,2X,'ATOL = ',E10.5/)
C
C   MAIN TIME INTEGRATION LOOP NEXT
C
      DO 150 IOUT = 1, NTIM
C
      CALL LSODI (RES,ADDA,DUMMY,NEQB,C,CDOTI,T,TOUT,ITOL,RTOL,ATOL,
*ITASK,ISTATE,IOPR,WORK,LRW,IWORK,LIW,MF)
C
      TMIN = T*A0/DP(1)/60.
C   TMIN IS THE DIMENSIONAL TIME IN MINUTES
C
      PRINT TMIN AND SOME LSODI DIAGNOSTICS
      WRITE (6,110) TMIN,RWORK(11),IWORK(14),IWORK(15),IWORK(11),
*IWORK(12),IWORK(13)
110  FORMAT (/2X,'CONCENTRATIONS AT TMIN = ',E11.4,3X,'HU = ',E12.5,2X,
*'NQU = ',J2,2X,'NQCUR = ',J2,2X,'NST = ',J5,2X,'NRE = ',J5,2X,'NJE = ',
*I5/)
C
      IF (IOUT.LT.NTIM) GO TO 140
C
      PRINT PARTICLE CONCENTRATIONS
      DO 120 J = 1, NRPT
      WRITE (6,130) (C(I+NSOR*(J-1)),I=1,NSOR)
120  CONTINUE
130  FORMAT (2X,5(E21.14,2X)/)
C
      PRINT FREE FLUID CONCENTRATION(S)
140  WRITE (6,130) (C(NEQBM+I),I=1,NSOR)
C
C   IF (ISTATE.LT.0) GO TO 160
      TOUT = T+DT
C
150  CONTINUE
C
      STOP
160  WRITE (6,170) ISTATE
170  FORMAT (/2X,'ERROR HALT...ISTATE = ',J3)
      STOP
      END
C
      SUBROUTINE RES (NEQB,T,C,S,R,IRES)
      DIMENSION C(NEQB),S(NEQB),R(NEQB)
      COMMON /BLK1/ CF1(5),CF2(5),DP(5),SH2(5),CO(5),EP,DR,DR2
      COMMON /BLK3/ NEQBM,NRPTM
      COMMON /BLK2/ AD(5,50),G(50),RPT(50)
C
C   THIS SUBROUTINE CALCULATES THE RESIDUAL FUNCTION REQUIRED BY LSODI
C   FIRST THE ELEMENTS OF THE DIAGONAL MATRIX "A" AND THE ELEMENTS OF
C   THE VECTOR "G" OF THE SYSTEM  $A \cdot DC/DT = G$  ARE CALCULATED. THEN THE
C   ELEMENTS ARE SCALED SO THAT THE MAGNITUDE OF THE LARGEST ELEMENT
C   ON ANY ROW IN "A" IS UNITY. THEN THE RESIDUALS  $R = G - A \cdot S$  WHERE S IS
C   AN INTERNALLY GENERATED APPROXIMATION TO DC/DT ARE CALCULATED. IN
C   ORDER TO MINIMIZE STORAGE ONLY THE NON-ZERO DIAGONALS OF "A"
C   ARE STORED BY PUTTING THEM IN A MATRIX "AD". THE ELEMENTS RELATE
C   VIS A VIS THE TRANSFORMATION  $A(I,J) = AD(I-J+MU+1,J)$ .
C
      NRPT = NRPTM+1
      NSOR = NEQBM/NRPT

```

```

MU = NSOR-1
NROWA = 2*NSOR-1
C
DO 30 N = 1, NRPT
C
DO 20 I = 1, NSOR
II = I+NSOR*(N-1)
C
DO 10 J = 1, NSOR
JJ = J+NSOR*(N-1)
K = II-JJ+MU+1
C
CALL DFDC (NSOR,NEQB,I,J,JJ,C,ACOE)
AD(K,JJ) = ACOEF/C0(1)
10 CONTINUE
C
AD(NSOR,II) = AD(NSOR,II)+EP*C0(I)/C0(1)
20 CONTINUE
C
30 CONTINUE
C
DO 40 II = 1, NSOR
AD(NSOR,NEQBM+II) = 1.0
40 CONTINUE
C
DO 80 N = 1, NRPT
C
DO 70 I = 1, NSOR
II = I+NSOR*(N-1)
C
IF (N.EQ.1) GO TO 50
IF (N.EQ.NRPT) GO TO 60
C
G(II) = CF2(I)*(C(II+NSOR)*(1./DR2+1./(DR*RPT(N)))+C(II)*(-2./DR2)
*+C(II-NSOR)*(1./DR2-1./(DR*RPT(N))))
GO TO 70
C
50 G(II) = 6*CF2(I)*(C(II+NSOR)-C(II))/DR2
GO TO 70
C
60 G(II) = CF2(I)*(-C(II)*2*SH2(I)*(1./(DR2*SH2(I))+1.+1./DR)+C(II-
*NSOR)*(2./DR2)+C(NEQBM+I)*(2.*SH2(I)*(1.+1./DR)))
C
70 CONTINUE
C
80 CONTINUE
C
DO 90 I = 1, NSOR
II = NEQBM+I
G(II) = CF1(I)*(C(II)-C(II-NSOR))
90 CONTINUE
C
DO 130 N = 1, NRPT
C
DO 120 I = 1, NSOR
II = I+NSOR*(N-1)
C
AII = 0.
DO 100 J = 1, NSOR
JJ = J+NSOR*(N-1)
K = II-JJ+MU+1

```

```

      IF (ABS(AD(K,JJ)).GT.AII) AII = ABS(AD(K,JJ))
100  CONTINUE
C
      DO 110 J = 1, NSOR
      JJ = J+NSOR*(N-1)
      K = II-JJ+MU+1
      AD(K,JJ) = AD(K,JJ)/AII
110  CONTINUE
C
      G(II) = G(II)/AII
120  CONTINUE
C
130  CONTINUE
C
      DO 160 N = 1, NRPT
C
      DO 150 I = 1, NSOR
      II = I+NSOR*(N-1)
      R(II) = 0.0
C
      DO 140 J = 1, NSOR
      JJ = J+NSOR*(N-1)
      K = II-JJ+MU+1
      R(II) = R(II)+AD(K,JJ)*S(JJ)
140  CONTINUE
C
      R(II) = G(II)-R(II)
150  CONTINUE
C
160  CONTINUE
C
      DO 170 I = 1, NSOR
      II = NEQBM+I
      R(II) = G(II)-AD(NSOR,II)*S(II)
170  CONTINUE
C
      RETURN
      END
C
      SUBROUTINE ADDA (NEQB,T,C,ML,MU,P,NROWP)
      DIMENSION C(NEQB),P(NROWP,NEQB)
      COMMON /BLK3/ NEQBM,NRPTM
      COMMON /BLK2/ AD(5,50),G(50),RPT(50)
C
C   THIS SUBROUTINE ADDS THE MATRIX "AD" TO THE CONTENTS OF THE ARRAY
C   "P" AS REQUIRED BY LSODI.
C
      NRPT = NRPTM+1
      NSOR = NEQBM/NRPT
      NROWA = 2*NSOR-1
C
      DO 10 I = 1, NROWA
      DO 10 J = 1, NEQB
      P(I,J) = P(I,J)+AD(I,J)
10  CONTINUE
C
      RETURN
      END
C
      SUBROUTINE DFDC (NSOR,NEQB,I,J,JJ,C,ACOE)
      DIMENSION C(NEQB)

```

COMMON /BLK1/ CF1(5),CF2(5),DP(5),SH2(5),C0(5),EP,DR,DR2

C THIS USER SUPPLIED SUBROUTINE PROVIDES PARTIAL DERIVATIVES OF THE
C DIMENSIONAL EQUILIBRIUM ISOTHERM(S) I.E. DF SUB I/ DC SUB J WHERE
C $F = F(\text{LOWER CASE C SUB 1, L.C. C SUB 2, ...})$ (WHERE LOWER CASE C
C DENOTES A DIMENSIONAL CONCENTRATION)
C $= F((\text{C SUB 1}) * C0(1), (\text{C SUB 2}) * C0(2), ...)$. ABSOLUTE VALUES OF
C CONCENTRATIONS ARE TAKEN TO AVOID PROBLEMS WITH OSCILLATIONS THAT
C MAY PRODUCE NEGATIVE VALUES EARLY IN THE CALCULATIONS.

C
C IF (I.EQ.1) GO TO 10
C IF (I.EQ.2) GO TO 40
10 IF (J.EQ.1) GO TO 20
C IF (J.EQ.2) GO TO 30

C
20 CD1 = ABS(C(JJ)*C0(J))
CD2 = ABS(C(JJ+1)*C0(J+1))
CJJ = ABS(C(JJ))
D1 = CD1**(.812)+.626*CD2**(.764)
ACOE = (1.29*C0(J)**(1.217)*CJJ**(.217)-.861*C0(J)**(2.029)*CJJ**
*(1.029)/D1)/D1
GO TO 70

C
30 CD1 = ABS(C(JJ-1)*C0(J-1))
CD2 = ABS(C(JJ)*C0(J))
CJJ = ABS(C(JJ))
CJ1 = ABS(C(JJ-1))
D1 = CD1**(.812)+.626*CD2**(.764)
ACOE = -.507*C0(J)**(.764)*C0(J-1)**(1.217)*CJJ**(-.236)*CJ1**(
*1.217)/(D1*D1)
GO TO 70

C
40 IF (J.EQ.1) GO TO 50
C IF (J.EQ.2) GO TO 60
50 CD1 = ABS(C(JJ)*C0(J))
CD2 = ABS(C(JJ+1)*C0(J+1))
CJJ = ABS(C(JJ))
CJ1 = ABS(C(JJ+1))
D2 = CD2**(.906)+.045*(CD1**(.634))
ACOE = -.031*C0(J)**(.634)*C0(J+1)**(1.254)*CJJ**(-.366)*CJ1**(
*1.254)/(D2*D2)
GO TO 70

C
60 CD1 = ABS(C(JJ-1)*C0(J-1))
CD2 = ABS(C(JJ)*C0(J))
CJJ = ABS(C(JJ))
D2 = CD2**(.906)+.045*(CD1**(.634))
ACOE = (1.342*C0(J)**(1.254)*CJJ**(.254)-.969*C0(J)**(2.160)*CJJ*
**(.160)/D2)/D2

C
70 RETURN
END

APPENDIX A.4 - SAMPLE INPUT FOR PROGRAM BATCH

.05,.94,.9859
.00000792,.00001464
.004472,.004132
.0005,.0005
5400.,100

APPENDIX A.5 - SAMPLE OUTPUT FROM PROGRAM BATCH

(NOTE: OUTPUT FORMAT ASSUMES 132 COLUMNS)

NUMBER OF SORBENTS = 2

PARTICLE DIFFUSIVITIES FILM COEFFICIENTS INITIAL BULK FLUID CONC.(G/CM**3) SHER-
WOOD NUMBER

.792000E-05	.447200E-02	.500000E-03	.600688E+02
.146400E-04	.413200E-02	.500000E-03	.300256E+02

R0 = .05000 A0 = .03142 EP = .94000 EB = .98590

DR = .100 RTOL = .10000E-03 ATOL = .10000E-05

CONCENTRATIONS AT TMIN = .0000E+00 HU = .00000E+00 NQU = 0 NQCUR = 0 NST = 0 NRE =
0 NJE = 0

.100000000000000E+01 .100000000000000E+01

CONCENTRATIONS AT TMIN = .9000E+00 HU = .12027E-02 NQU = 4 NQCUR = 4 NST = 33 NRE =
101 NJE = 12

.86953593640663E+00 .85219588655755E+00

CONCENTRATIONS AT TMIN = .1800E+01 HU = .22006E-02 NQU = 3 NQCUR = 3 NST = 41 NRE =
120 NJE = 14

.83281608932349E+00 .77798884400585E+00

CONCENTRATIONS AT TMIN = .8820E+02 HU = .14661E-01 NQU = 2 NQCUR = 2 NST = 164 NRE =
456 NJE = 31

.40831360772430E+00 .24710538873845E+00

CONCENTRATIONS AT TMIN = .8910E+02 HU = .19003E-01 NQU = 2 NQCUR = 2 NST = 165 NRE =
459 NJE = 31

.40783219174264E+00 .24670564053474E+00

CONCENTRATIONS AT TMIN = .9000E+02 HU = .19003E-01 NQU = 2 NQCUR = 2 NST = 165 NRE =
459 NJE = 31

.31729516310724E+00	.16878864561401E+00
.31885285621030E+00	.17084055467294E+00
.32380873045611E+00	.17679183900218E+00
.33159417010609E+00	.18558677206935E+00
.34163623728899E+00	.19604534865549E+00
.35312694116668E+00	.20700859812083E+00
.36519739194929E+00	.21751914684515E+00
.37704160980992E+00	.22686730303422E+00
.38797959773639E+00	.23458565685560E+00
.39748865912830E+00	.24042863471792E+00
.40515818134874E+00	.24432783946658E+00
.40736800294834E+00	.24631909109447E+00

APPENDIX A.6 - COLUMN SIMULATOR CODE

```

PROGRAM COLUM (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C THIS IS THE MAIN PROGRAM FOR THE COLUMN SIMULATOR. IT HAS BEEN
C WRITTEN FOR USE WITH LSODI (LIVERMORE SOLVER FOR ORDINARY
C DIFFERENTIAL EQUATIONS (IMPLICIT FORM) MARCH 30, 1987 VERSION)
C WHICH CAN BE USED TO SOLVE INITIAL VALUE PROBLEMS FOR LINEARLY
C IMPLICIT FIRST ORDER DIFFERENTIAL EQUATIONS OF THE GENERAL
C FORM  $AD(T,Y)*DY/DT=G(T,Y)$ .
C
C MOST OF THE PROGRAM VARIABLES ARE DEFINED IN THE ACCOMPANYING
C REPORT OR THE LSODI MANUAL. THOSE FEW THAT ARE NOT AND ARE NOT
C OBVIOUS ARE DESCRIBED AS THEY ARE DEFINED IN THE PROGRAM.
C
C NOTE THAT  $NEQC=NSOR*(NRPT+1)*MXPT$  - MAKE SURE THAT THE DIMENSIONS
C OF AD AND G BELOW ARE AT LEAST  $AD(5,NEQC)$  AND  $G(NEQC)$ .
C ALSO  $LRW=$ DIMENSION OF VECTOR RWORK
C  $=.GE.22+17*NEQC+(2*ML+MU)*NEQC$  FOR  $MF=15$ 
C  $LIW=$ DIMENSION OF VECTOR IWORK
C  $=.GE.20+NEQC$ 
C
C PARAMETER (NSOR=3,NRPT=6,MXPT=10,NEQC=210)
C EXTERNAL RES,ADDA
C DIMENSION C(NEQC),CDOTI(NEQC),RWORK(9000),IWORK(400)
C COMMON /BLK1/ CF1(5),CF2(5),CF3(5),DP(5),DL(5),SH2(5),C0(5),CIN(5)
C *PE(5),EP,DR,DR2,DX,DX2
C COMMON /BLK2/ AD(5,400),G(400),RPT(50)
C COMMON /BLK3/ NEQB,NEQBM,NRPTM,MXPTM
C REAL KF(5),LEN
C
C PI = 3.1415926535897
C NEQB = NSOR*(NRPT+1)
C NEQBM = NEQB-NSOR
C NEQCM = NEQC-NSOR
C NRPTM = NRPT-1
C MXPTM = MXPT-1
C
C READ PARTICLE RADIUS AND VOID FRACTION AND BED VOID FRACTION
C READ (5,*) R0,EP,EB
C  $A0 = 4*PI*R0**2$ 
C
C READ PARTICLE DIFFUSIVITIES, AXIAL DIFFUSIVITIES, FILM MASS
C TRANSFER COEFFICIENTS AND INITIAL DIMENSIONAL BULK CONCENTRATIONS
C READ (5,*) (DP(L),L=1,NSOR)
C READ (5,*) (DL(L),L=1,NSOR)
C READ (5,*) (KF(L),L=1,NSOR)
C READ (5,*) (C0(L),L=1,NSOR)
C
C READ COLUMN LENGTH AND SUPERFICIAL FEEDSTREAM VELOCITY
C READ (5,*) LEN,VEL
C
C READ TOTAL SIMULATION TIME IN SECONDS AND NUMBER OF EQUALLY
C SPACED TIME STEPS AT WHICH OUTPUT IS DESIRED (SEE NFLAG BELOW)
C READ (5,*) TSEC,NTSTEPS
C
C TMAX = TSEC*DP(1)/A0
C DT = TMAX/NTSTEPS
C TMAX IS THE TOTAL NON-DIMENSIONAL SIMULATION TIME
C
C READ (5,*) NFLAG

```

```

C IF NFLAG.EQ.0 COMPUTATIONS START AT NON-DIMENSIONAL TIME T=0.0
C IF NFLAG.NE.0 SIMULATION WILL CONTINUE FROM SOME T.GT.0.0 USING
C INPUT VALUES OF THE CONCENTRATIONS THAT HAVE BEEN DETERMINED IN
C A PREVIOUS RUN AND HAVE BEEN APPENDED FROM THE PREVIOUS OUTPUT
C FILE TO THE CURRENT INPUT FILE USING A TEXT EDITOR.
C
C   DEFINE SOME CONVENIENT COEFFICIENTS
DO 10 L = 1, NSOR
  CIN(L) = C0(L)
  CF1(L) = (EB-1.)*KF(L)*3*A0/(EB*DP(1)*R0)
  CF2(L) = 4*PI*EP*DP(L)*C0(L)/(DP(1)*C0(1))
  CF3(L) = A0*VEL/(LEN*EB*DP(1))
  PE(L) = LEN*VEL/(EB*DL(L))
  SH2(L) = 2*R0*KF(L)/(EP*DP(L))
10 CONTINUE
C
C   PRINT OUT INPUT PARAMETERS AND REDEFINE SH2
WRITE (6,20) NSOR
20 FORMAT (2X,'NUMBER OF SORBENTS = ',I2,/)
WRITE (6,30)
30 FORMAT (2X,'DP',14X,'DL',14X,'KF',14X,'C0',14X,'SH ',14X,'PE')
C
DO 40 L = 1, NSOR
  WRITE (6,50) DP(L),DL(L),KF(L),C0(L),SH2(L),PE(L)
  SH2(L) = SH2(L)/2.
40 CONTINUE
50 FORMAT (2X,6(E12.6,4X),/)
C
WRITE (6,60) R0,A0,EP,EB,LEN,VEL
60 FORMAT (/2X,'R0 = ',F8.5,2X,'A0 = ',F8.5,2X,'EP = ',F8.5,2X,'EB = ',
* ',F8.5,2X,'LEN = ',F8.5,2X,'VEL = ',F8.5,/)
C
C   SET RADIAL GRID SIZE AND RADIAL GRID POINTS
DR = 1./FLOAT(NRPTM)
DR2 = DR*DR
DO 70 N = 1, NRPT
  RPT(N) = (N-1)*DR
70 CONTINUE
C
C   SET AXIAL GRID SIZE
DX = 1./FLOAT(MXPTM)
DX2 = DX*DX
C
C   SET INITIAL DIMENSIONLESS PARTICLE AND BULK CONCENTRATIONS
IF (NFLAG.EQ.0) THEN
  T = 0.0
  DO 110 M = 1, MXPT
    DO 90 N = 1, NRPT
      DO 80 I = 1, NSOR
        II = I+NSOR*(N-1)+NEQB*(M-1)
        C(II) = 1.E-13
80 CONTINUE
90 CONTINUE
      DO 100 I = 1, NSOR
        C(NEQBM+I+NEQB*(M-1)) = 1.E-13
100 CONTINUE
110 CONTINUE
      ELSE
        READ (5,130) T
        DO 120 L = 1, NEQC
          READ (5,130) C(L)

```

```

120 CONTINUE
    ENDIF
130 FORMAT (2X,E21.14)
C
C SET INPUTS FOR LSODI - SEE LSODI MANUAL
NTIM = NTSTEPS+1
ITASK = 1
ML = NSOR-1
MU = NSOR-1
IWORK(1) = ML
IWORK(2) = MU
MF = 15
ISTATE = 0
IOPT = 1
RWORK(5) = 0.0
RWORK(6) = 0.0
RWORK(7) = 0.0
RWORK(8) = 0.0
RWORK(9) = 0.0
RWORK(10) = 0.0
IWORK(5) = 0
IWORK(6) = 600
IWORK(7) = 0
IWORK(8) = 0
IWORK(9) = 0
IWORK(10) = 0
LRW = 9000
LIW = 400
TOUT = T
RTOL = 1.E-04
ATOL = 1.E-06
ITOL = 1
C
C WRITE (6,140) DR,DX,RTOL,ATOL
140 FORMAT (/2X,'DR = ',F6.3,2X,'DX = ',F6.3,2X,'RTOL = ',E10.5,2X,'A
    *TOL = ',E10.5,/)
C
C TIME INTEGRATION LOOP NEXT
C
DO 240 IOUT = 1, NTIM
C
CALL LSODI (RES,ADDA,DUMMY,NEQC,C,CDOTI,T,TOUT,ITOL,RTOL,ATOL,
    *ITASK,ISTATE,IOPT,RWORK,LRW,IWORK,LIW,MF)
C
TMIN = T*A0/DP(1)/60.
C
TMIN IS DIMENSIONAL TIME IN MINUTES
C
C PRINT TMIN AND SOME LSODI DIAGNOSTICS
WRITE (6,150) TMIN,RWORK(11),IWORK(14),IWORK(15),IWORK(11),
    *IWORK(12),IWORK(13)
150 FORMAT (/2X,'CONCENTRATIONS AT TMIN = ',E11.4,3X,'HU = ',E12.5,2X,
    *'NQU = ',I2,2X,'NQCUR = ',I2,2X,'NST = ',I5,2X,'NRE = ',I5,2X,'NJE = ',
    *I5,/)
C
IF (IOUT.LT.NTIM) GO TO 180
C
C PRINT ALL PARTICLE AND FREE FLUID CONCENTRATIONS
DO 170 I = 1, NSOR
DO 160 M = 1, MXPT
WRITE (6,200) (C(I+NSOR*(N-1)+NEQB*(M-1)),N=1,NRPT),C(NEQBM+I+NEQB
    ** (M-1))

```

```

160 CONTINUE
    WRITE (6,190)
170 CONTINUE
    GO TO 210
C
C PRINT OUTLET CONCENTRATIONS
180 WRITE (6,200) (C(NEQCM+I),I=1,NSOR)
C
190 FORMAT (/)
200 FORMAT (2X,12(E10.4,1X))
C
C PRINT NON-DIMENSIONAL TIME AND ALL CONCENTRATIONS AT END OF RUN
C IN HIGH PRECISION FOR USE AS INPUT FOR ANY EXTENSION OF THE RUN
210 IF (IOUT.EQ.NTIM) THEN
    WRITE (6,130) T
    DO 220 L = 1, NEQC
        WRITE (6,130) C(L)
220 CONTINUE
    ELSE
        GO TO 230
    ENDIF
C
230 IF (ISTATE.LT.0) GO TO 250
    TOUT = TOUT+DT
C
240 CONTINUE
C
    STOP
250 WRITE (6,260) ISTATE
260 FORMAT (/,2X,'ERROR HALT...ISTATE = ',I3)
    STOP
    END
C
    SUBROUTINE RES (NEQC,T,C,S,R,IRES)
    DIMENSION C(NEQC),S(NEQC),R(NEQC)
    COMMON /BLK1/ CF1(5),CF2(5),CF3(5),DP(5),DL(5),SH2(5),C0(5),CIN(5)
    *PE(5),EP,DR,DR2,DX,DX2
    COMMON /BLK3/ NEQB,NEQBM,NRPTM,MXPTM
    COMMON /BLK2/ AD(5,400),G(400),RPT(50)
C
C THIS SUBROUTINE CALCULATES THE RESIDUAL FUNCTION REQUIRED BY LSODI
C FIRST THE ELEMENTS OF THE DIAGONAL MATRIX "A" AND THE ELEMENTS OF
C THE VECTOR "G" OF THE SYSTEM  $A \cdot DC/DT = G$  ARE CALCULATED. THEN THE
C ELEMENTS ARE SCALED SO THAT THE MAGNITUDE OF THE LARGEST ELEMENT
C ON ANY ROW IN "A" IS UNITY. THEN THE RESIDUALS  $R = G - A \cdot S$  WHERE S IS
C AN INTERNALLY GENERATED APPROXIMATION TO  $DC/DT$  ARE CALCULATED. IN
C ORDER TO MINIMIZE STORAGE ONLY THE NON-ZERO DIAGONALS OF "A"
C ARE STORED BY PUTTING THEM IN A MATRIX "AD". THE ELEMENTS RELATE
C VIS A VIS THE TRANSFORMATION  $A(I,J) = AD(I-J+MU+1,J)$ .
C
    NRPT = NRPTM+1
    MXPT = MXPTM+1
    NSOR = NEQBM/NRPT
    MU = NSOR-1
    NROWA = 2*NSOR-1
C
    IF (T.GT.0.0) GO TO 20
    DO 10 II = 1, NROWA
        DO 10 JJ = 1, NEQC
            AD(II,JJ) = 0.0

```

```

10 CONTINUE
C
20 DO 70 M = 1, MXPT
C
DO 50 N = 1, NRPT
C
DO 40 I = 1, NSOR
II = I+NSOR*(N-1)+NEQB*(M-1)
C
DO 30 J = 1, NSOR
JJ = J+NSOR*(N-1)+NEQB*(M-1)
K = II-JJ+MU+1
C
CALL DFDC (NEQC,I,J,JJ,C,ACOE)
C
AD(K,JJ) = ACOEF/C0(1)
30 CONTINUE
C
AD(NSOR,II) = AD(NSOR,II)+EP*C0(I)/C0(1)
40 CONTINUE
C
50 CONTINUE
C
DO 60 I = 1, NSOR
AD(NSOR,NEQBM+I+NEQB*(M-1)) = 1.0
60 CONTINUE
C
70 CONTINUE
C
DO 150 M = 1, MXPT
C
DO 110 N = 1, NRPT
C
DO 100 I = 1, NSOR
II = I+NSOR*(N-1)+NEQB*(M-1)
C
IF (N.EQ.1) GO TO 80
IF (N.EQ.NRPT) GO TO 90
C
G(II) = CF2(I)*(C(II+NSOR)*(1./DR2+1./(DR*RPT(N)))+C(II)*(-2./DR2)
*+C(II-NSOR)*(1./DR2-1./(DR*RPT(N))))
GO TO 100
C
80 G(II) = 6*CF2(I)*(C(II+NSOR)-C(II))/DR2
GO TO 100
C
90 CBD = C(NEQBM+I+NEQB*(M-1))
G(I,I) = CF2(I)*(-C(II)*2*SH2(I)*(1./(DR2*SH2(I))+1.+1./DR)+C(II-
*NSOR)*(2./DR2)+CBD*(2.*SH2(I)*(1.+1./DR)))
C
100 CONTINUE
C
110 CONTINUE
C
DO 140 I = 1, NSOR
II = NEQBM+I+NEQB*(M-1)
C
IF (M.EQ.1) GO TO 120
IF (M.EQ.MXPT) GO TO 130
C
G(II) = CF1(I)*(C(II)-C(II-NSOR))+CF3(I)*((C(II+NEQB)-2*C(II)+C(II

```

```

      *-NEQB))/(PE(I)*DX2)-(C(II)-C(II-NEQB))/(DX))
      GO TO 140
C
120 G(II) = CF1(I)*(C(II)-C(II-NSOR))+CF3(I)*(2*(C(II+NEQB)-C(II)*(1.+
      *DX*PE(I))+DX*PE(I)*CIN(I)/C0(I))/(PE(I)*DX2)-PE(I)*(C(II)-CIN(I)/
      *C0(I)))
      GO TO 140
C
130 IIM = II-NEQB
      IIM2 = IIM-NEQB
      IF (C(II).LT.1.E-08) THEN
        G(II) = CF1(I)*(C(II)-C(II-NSOR))+CF3(I)*2*(C(IIM)-C(II))/(PE(I)*
        *DX2)
C      THIS BOUNDARY TREATMENT IS USED EARLY IN THE CALCULATIONS TO
C      REDUCE OR ELIMINATE THE POSSIBILITY OF NEGATIVE OUTLET VALUES
C      AS DESCRIBED IN THE ACCOMPANYING REPORT
      ELSE
        G(II) = (4*G(IIM)-G(IIM2))/3.
      ENDIF
C
140 CONTINUE
C
150 CONTINUE
C
      DO 200 M = 1, MXPT
C
      DO 190 N = 1, NRPT
C
      DO 180 I = 1, NSOR
        II = I+NSOR*(N-1)+NEQB*(M-1)
C
        AII = 0.
        DO 160 J = 1, NSOR
          JJ = J+NSOR*(N-1)+NEQB*(M-1)
          K = II-JJ+MU+1
          IF (ABS(AD(K,JJ)).GT.AII) AII = ABS(AD(K,JJ))
160 CONTINUE
C
          DO 170 J = 1, NSOR
            JJ = J+NSOR*(N-1)+NEQB*(M-1)
            K = II-JJ+MU+1
            AD(K,JJ) = AD(K,JJ)/AII
170 CONTINUE
C
            G(II) = G(II)/AII
180 CONTINUE
C
190 CONTINUE
C
200 CONTINUE
C
      DO 250 M = 1, MXPT
C
      DO 230 N = 1, NRPT
C
      DO 220 I = 1, NSOR
        II = I+NSOR*(N-1)+NEQB*(M-1)
        R(II) = 0.0
C
        DO 210 J = 1, NSOR
          JJ = J+NSOR*(N-1)+NEQB*(M-1)

```

```

      K = II-JJ+MU+1
      R(II) = R(II)+AD(K,II)*S(JJ)
210  CONTINUE
C
      R(II) = G(II)-R(II)
220  CONTINUE
C
230  CONTINUE
C
      DO 240 I = 1, NSOR
      II = NEQBM+I+NEQB*(M-1)
      R(II) = G(II)-AD(NSOR,II)*S(II)
240  CONTINUE
C
250  CONTINUE
C
      RETURN
      END
C
      SUBROUTINE ADDA (NEQC,T,C,ML,MU,P,NROWP)
      DIMENSION C(NEQC),P(NROWP,NEQC)
      COMMON /BLK3/ NEQB,NEQBM,NRPTM,MXPTM
      COMMON /BLK2/ AD(5,400),G(400),RPT(50)
C
C   THIS SUBROUTINE ADDS THE MATRIX "AD" TO THE CONTENTS OF THE ARRAY
C   "P" AS REQUIRED BY LSODI.
C
      NRPT = NRPTM+1
      NSOR = NEQBM/NRPT
      NROWA = 2*NSOR-1
C
      DO 10 I = 1, NROWA
      DO 10 J = 1, NEQC
      P(I,J) = P(I,J)+AD(I,J)
10   CONTINUE
C
      RETURN
      END
C
      SUBROUTINE DFDC (NEQC,I,J,II,C,ACOE)
      DIMENSION C(NEQC)
      COMMON /BLK1/ CF1(5),CF2(5),CF3(5),DP(5),DL(5),SH2(5),C0(5),CIN(5)
      * ,PE(5),EP,DR,DR2,DX,DX2
C
C   THIS USER SUPPLIED SUBROUTINE PROVIDES PARTIAL DERIVATIVES OF THE
C   DIMENSIONAL EQUILIBRIUM ISOTHERM(S) I.E. DF SUB I/ DC SUB J WHERE
C   F=F(LOWER CASE C SUB 1,L.C. C SUB 2,....) (WHERE LOWER CASE C
C   DENOTES A DIMENSIONAL CONCENTRATION)
C   =F((C SUB 1)*C0(1), (C SUB 2)*C0(2),....). ABSOLUTE VALUES OF
C   CONCENTRATIONS ARE TAKEN TO AVOID PROBLEMS WITH OSCILLATIONS THAT
C   MAY PRODUCE NEGATIVE VALUES EARLY IN THE CALCULATIONS.
C
      IF (I.EQ.2) GO TO 10
      IF (I.EQ.3) GO TO 20
C
      IF (J.EQ.1) THEN
      CD1 = ABS(C(JJ)*C0(1))
      CD2 = ABS(C(JJ+1)*C0(2))
      CD3 = ABS(C(JJ+2)*C0(3))
      CJJ = ABS(C(JJ))
      D1 = CD1**(.73)+1.44*CD2**(.793)+.53*CD3**(.467)

```

```

ACOE = (1.191*C0(1)**(1.134)*CJJ**(.134)-.767*C0(1)**(1.864)*CJJ*
**(.864)/D1)/D1
ELSE
IF (J.EQ.2) THEN
CD1 = ABS(C(JJ-1)*C0(1))
CD2 = ABS(C(JJ)*C0(2))
CD3 = ABS(C(JJ+1)*C0(3))
CJJ = ABS(C(JJ))
D1 = CD1**(.73)+1.44*CD2**(.793)+.53*CD3**(.467)
ACOE = -1.199*CD1**(.134)*C0(2)**.793*CJJ**(-.207)/(D1*D1)
ELSE
CD1 = ABS(C(JJ-2)*C0(1))
CD2 = ABS(C(JJ-1)*C0(2))
CD3 = ABS(C(JJ)*C0(3))
CJJ = ABS(C(JJ))
D1 = CD1**(.73)+1.44*CD2**(.793)+.53*CD3**(.467)
ACOE = -.26*CD1**(.134)*C0(3)**(.467)*CJJ**(-.533)/(D1*D1)
ENDIF
ENDIF
GO TO 30

```

C

```

10 IF (J.EQ.1) THEN
CD1 = ABS(C(JJ)*C0(1))
CD2 = ABS(C(JJ+1)*C0(2))
CD3 = ABS(C(JJ+2)*C0(3))
CJJ = ABS(C(JJ))
D2 = CD2**(.831)+.52*CD1**(.884)+.30*CD3**(.536)
ACOE = -.501*C0(1)**(.884)*CJJ**(-.116)*CD2**(.182)/(D2*D2)
ELSE
IF (J.EQ.2) THEN
CD1 = ABS(C(JJ-1)*C0(1))
CD2 = ABS(C(JJ)*C0(2))
CD3 = ABS(C(JJ+1)*C0(3))
CJJ = ABS(C(JJ))
D2 = CD2**(.831)+.52*CD1**(.884)+.30*CD3**(.536)
ACOE = (1.288*C0(2)**(1.182)*CJJ**(.182)-.906*C0(2)**(2.013)*CJJ*
**(.1013)/D2)/D2
ELSE
CD1 = ABS(C(JJ-2)*C0(1))
CD2 = ABS(C(JJ-1)*C0(2))
CD3 = ABS(C(JJ)*C0(3))
CJJ = ABS(C(JJ))
D2 = CD2**(.831)+.52*CD1**(.884)+.30*CD3**(.536)
ACOE = -.175*CD2**(.182)*C0(3)**(.536)*CJJ**(-.464)/(D2*D2)
ENDIF
ENDIF
GO TO 30

```

C

```

20 IF (J.EQ.1) THEN
CD1 = ABS(C(JJ)*C0(1))
CD2 = ABS(C(JJ+1)*C0(2))
CD3 = ABS(C(JJ+2)*C0(3))
CJJ = ABS(C(JJ))
D3 = CD3**(.002)+1.07*CD1**(.286)+.79*CD2**(.235)
ACOE = -.242*CD3**(.224)*C0(1)**(.286)*CJJ**(-.714)/(D3*D3)
ELSE
IF (J.EQ.2) THEN
CD1 = ABS(C(JJ-1)*C0(1))
CD2 = ABS(C(JJ)*C0(2))
CD3 = ABS(C(JJ+1)*C0(3))
CJJ = ABS(C(JJ))

```

```

D3 = CD3**(.002)+1.07*CD1**(.286)+.79*CD2**(.235)
ACOE = -.147*CD3**(.224)*C0(2)**(.235)*CJJ**(-.765)/(D3*D3)
ELSE
CD1 = ABS(C(JJ-2)*C0(1))
CD2 = ABS(C(JJ-1)*C0(2))
CD3 = ABS(C(JJ)*C0(3))
CJJ = ABS(C(JJ))
D3 = CD3**(.002)+1.07*CD1**(.286)+.79*CD2**(.235)
ACOE = (.177*C0(3)**(.224)*CJJ**(-.776)-.002*C0(3)**(.226)*CJJ**(-.774)/D3)/D3
ENDIF
ENDIF

```

```

C
30 RETURN
END

```

APPENDIX A.7 - SAMPLE INPUT FOR PROGRAM COLUM

.05,.94,.45
.00000760,.00001270,.00001920
.04,.04,.04
.00212,.00195,.00217
.000915,.000912,.000997
20.5,.14
16535,.100
0

APPENDIX A.8 - SAMPLE OUTPUT FROM PROGRAM COLUM

(NOTE: OUTPUT FORMAT ASSUMES 132 COLUMNS)

NUMBER OF SORBENTS = 3

DP	DL	KF	C0	SH	PE		
.760000E-05	.400000E-01	.212000E-02	.915000E-03	.296753E+02	.159444E+03		
.127000E-04	.400000E-01	.195000E-02	.912000E-03	.163344E+02	.159444E+03		
.192000E-04	.400000E-01	.217000E-02	.997000E-03	.120235E+02	.159444E+03		

R0 = .05000 A0 = .03142 EP = .94000 EB = .45000 LEN = 20.50000 VEL = .14000

DR = .200 DX = .111 RTOL = .10000E-03 ATOL = .10000E-05

CONCENTRATIONS AT TMIN = .0000E+00 HU = .00000E+00 NQU = 0 NQCUR = 0 NST = 0 NRE =
0 NJE = 0

.1000E-12 .1000E-12 .1000E-12

CONCENTRATIONS AT TMIN = .2756E+01 HU = .93098E-03 NQU = 2 NQCUR = 2 NST = 137 NRE =
577 NJE = 57

.2625E-02 .2938E-02 .1424E-02

CONCENTRATIONS AT TMIN = .5512E+01 HU = .74779E-03 NQU = 2 NQCUR = 2 NST = 191 NRE =
831 NJE = 82

.7336E-02 .5725E-02 .1553E-02

.
.
.
.
.

CONCENTRATIONS AT TMIN = .2701E+03 HU = .95186E-03 NQU = 2 NQCUR = 2 NST = 5713 NRE =
27175 NJE = 2859

.9959E+00 .1016E+01 .9865E+00

CONCENTRATIONS AT TMIN = .2728E+03 HU = .95177E-03 NQU = 2 NQCUR = 2 NST = 5769 NRE =
27429 NJE = 2886

.9958E+00 .1015E+01 .9882E+00

CONCENTRATIONS AT TMIN = .2756E+03 HU = .47589E-03 NQU = 2 NQCUR = 2 NST = 5825 NRE
=27698 NJE = 2915

.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1001E+01 .1001E+01 .1001E+01 .1001E+01 .1000E+01 .1000E+01 .1000E+01
.1003E+01 .1003E+01 .1002E+01 .1002E+01 .1001E+01 .1001E+01 .1000E+01
.1008E+01 .1008E+01 .1007E+01 .1005E+01 .1003E+01 .1001E+01 .1001E+01
.1005E+01 .1005E+01 .1003E+01 .1001E+01 .9988E+00 .9963E+00 .9954E+00

.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1001E+01 .1001E+01 .1001E+01 .1001E+01 .1001E+01 .1000E+01 .1000E+01
.1003E+01 .1003E+01 .1003E+01 .1002E+01 .1002E+01 .1001E+01 .1001E+01
.1009E+01 .1009E+01 .1008E+01 .1006E+01 .1005E+01 .1003E+01 .1002E+01
.1022E+01 .1021E+01 .1019E+01 .1016E+01 .1012E+01 .1008E+01 .1005E+01
.1051E+01 .1049E+01 .1044E+01 .1037E+01 .1027E+01 .1017E+01 .1011E+01
.1063E+01 .1061E+01 .1055E+01 .1045E+01 .1033E+01 .1020E+01 .1013E+01

.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.9999E+00 .9999E+00 .1000E+01 .1000E+01 .1000E+01 .1000E+01 .1000E+01
.9998E+00 .9998E+00 .9998E+00 .9999E+00 .9999E+00 .9999E+00 .9999E+00
.9994E+00 .9994E+00 .9995E+00 .9995E+00 .9996E+00 .9997E+00 .9998E+00
.9982E+00 .9983E+00 .9984E+00 .9987E+00 .9989E+00 .9992E+00 .9995E+00
.9952E+00 .9954E+00 .9958E+00 .9964E+00 .9971E+00 .9979E+00 .9986E+00
.9875E+00 .9879E+00 .9889E+00 .9904E+00 .9924E+00 .9946E+00 .9964E+00
.9698E+00 .9706E+00 .9731E+00 .9770E+00 .9818E+00 .9870E+00 .9914E+00
.9622E+00 .9633E+00 .9665E+00 .9714E+00 .9775E+00 .9841E+00 .9894E+00

.40000730157174E+01
.99999999032061E+00
.10000003132272E+01

.99542099063591E+00
.10127930236785E+01
.98935079600005E+00

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